THE JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR

Volume 7, 1952

November - December

Issue 6

IN ENGLISH TRANSLATION

CONSULTANTS BUREAU
152 West 42 nd St., New York 18, N.Y.

—An agency for the interpretation of international knowledge—

The Journal of Analytical Chemistry of the U.S.S.R. in English Translation,

November - December, 1952

TABLE OF CONTENTS

	Page	Russ. page
1. Carry the Banner of Soviet Science Proudly.....	359	323
2. The Application of Mathematical Statistics in Analytical Chemistry. N. P. Komar.....	361	325
3. The Ultramicro Method of Chemical Analysis. Part I. I. P. Alimarin and M. N. Petrikova.....	377	341
4. Spectrophotometry in Chemical Analysis. S. I. Sinyakova and N. P. Ivanov.....	385	349
5. Quantitative X-Ray Spectrographic Analysis. Part I. E. E. Vainshtein, I. D. Shevaleevsky, and M. M. Kakhana....	403	363
6. Application of the Ion-Exchange Chromatographic Method in the Analysis of Copper Iron Ceramic Alloys and Bronzes. D. I. Ryabchikov and V. E. Bukhtiarov.....	377	377
Chronicle		
7. Alexei Mikhailovich Vasilev (on his 70th birthday).....	425	384
Criticism		
8. A New and Useful Book. "A Collection of Problems, Exercises, and Questions in Qualitative Analysis", by N. P. Komar. Reviewed by V. V. Shcherbina.....	429	386

THE JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR

Volume VII (1952)

Number 6 (November - December)

(A publication of the Academy of Sciences of the U.S.S.R.

IN ENGLISH TRANSLATION

Copyright, 1953

CONSULTANTS BUREAU

152 West 42nd Street
New York 18, N. Y.

Printed in Great Britain

Annual subscription $80.00.
Single issue 20.00

Note: The sale of photostatic copies of any portion of this copyright translation is expressly prohibited by the copyright owners. A complete copy of any paper in this issue may be purchased from the publisher for $7.50.

CARRY THE BANNER OF SOVIET SCIENCE PROUDLY

The historical resolutions of the XIX Congress of the Communist Party of the Soviet Union open up new, boundless horizons for scientific and practical activity before the analytical chemists of our country.

The gigantic developments of industry provided for by the directives of the Congress, the huge increase in work on the study of the mineral resources of our country, and the use of its immense natural resources, the construction of the colossal undertakings for the production of energy, the increase in agricultural production and much else - all require a considerable increase in analytical chemical work, the setting up of new analytical laboratories; it is necessary to solve a number of new problems in science, to improve available methods of analytical control already in use and to develop new ones; to construct new apparatus, to discover new reagents; to examine existing theoretical principles critically, and to develop new theories in analytical chemistry in the light of dialectical materialism; to produce special textbooks and monographs on analytical chemistry.

The necessity of satisfying the analytical requirements of all sections of our socialist economy places an honorable and responsible task before Soviet analysts.

It is essential to develop both the theoretical and practical analytical chemistry of low concentrations of elements - the chemistry of traces. It is essential to develop methods for the separation and concentration of elements from their very dilute solutions - extraction methods, the application of ion exchange resins and of radioactive indicators, etc..

Much contemporary analytical chemistry is far from satisfactory with respect to the rapidity with which an analysis can be carried out. The development of new and the improvement of existing rapid methods of analysis is one of the most important problems of our analysts. Despite the widespread introduction of physical and instrumental methods of analysis, the development of purely chemical, preparatory operations and methods of analysis should not be ignored. In the field of physical and physico-chemical instruments, complex work and further improvements and developments of new forms of available apparatus comes first. It is necessary to introduce automatics positively into analytical chemistry, and to develop automatic and semi-automatic apparatus for chemical analysis.

Our analysts have discovered many new analytical reagents, mainly organic reagents, many of which are nowadays used in analytical laboratories all over the world. It is necessary to continue this glorious tradition of Russian analysts and to discover new analytical reagents on the basis of the theory of their action developed by Soviet scientists, and to continue to develop their theory.

Although there are numbers of fine examples of newly developed analytical methods being rapidly introduced into practice, there are still many cases where this is not true.

In such cases it is necessary to deal resolutely, remembering that there is no point in working out an analytical method which cannot find practical application.

One of the reasons which hinders the introduction of better methods is the lack of a sufficient amount of coordinating work on analytical chemistry between Institute and Factory laboratories, and another is the sometimes unsatisfactory state of the organization of technical information.

We must first of all raise the cultural level of the workers in chemical-analytical, and control laboratories in our factories and set up research groups of analytical chemists in our large factories.

It is necessary to attract more average chemical personnel with a good specialist background for carrying out established analytical control operations. Highly qualified analysts should be given chances to improve their knowledge by means of specialist courses.

During the fifth Five Year Plan the number of young specialists will increase considerably. A large army of young specialists will enter analytical laboratories and Institutions. Older analytical chemists should consider it an honorable task to help these young analysts to organize their work correctly.

Chemical industry and the apparatus manufacturers should satisfy the new requirements of chemists, research workers, and others.

The advance of our science will be slow if we do not maintain a creative exchange of opinion and keep up criticism and self criticism as Comrade Stalin has often pointed out to us.

The Communist party and the Soviet Government show immense trust and support for the scientists of our country. In its directive the XIX Congress remarks:

"Assist the scientist in every way to develop his theoretical problems in all branches of knowledge and strengthen the bond between science and production".

By active, selfless work on his part the Soviet analytical chemist should promote the solution of the miscellaneous problems which crop up as a result of the Five Year Plans and speed up the fulfilment of the Stalin program for the gradual transition from Socialism to Communism.

Soviet analysts must respond with all their strength so that they can repay honorably the trust placed in them, and proudly carry the banner of Soviet science in order that Soviet analytical chemistry together with Soviet science may occupy the first place in the world.

THE APPLICATION OF MATHEMATICAL STATISTICS IN ANALYTICAL CHEMISTRY

N.P.Komar

A. M. Gorky Kharkhov State University

The directives of the XIX Congress of the party regarding the fifth Five Year Plan for the development of the USSR in the period 1951-1955 have placed a number of new and important problems and tasks before the chemists of our country. The fulfilment of these new problems is impossible without a scientifically organized control of all productive operations and in this sense every line of the directives is full of deep import for both those chemists participating directly in production control, and those working out the principles and theoretical details of the theory of analytical chemistry, and new analytical methods.

In the epoch of the great Stalin projects, analysts will have to solve the problems which confront them more accurately and more rapidly than hitherto. Our responsibility for the quality of our work will increase daily and we shall have to adopt all measures possible to improve our work.

In particular it is very important to use the methods of mathematical statistics and the theory of errors on an even wider scale, since they can be of immense value for the selection of new analytical procedures and their development, for the evaluation of analytical results and for the organization of the control of work of any analytical laboratory in the USSR.

The use of mathematical statistics in analytical chemistry is fundamentally sound, since an analyst's work is the sum total of a number of similar operations; weighings, titrations, determinations of optical density, etc.. In order to carry out these operations, various types of apparatus are used, among which it is possible to distinguish individual combinations of similar apparatuses, e.g. analytical weights, pipets, burets, etc.. In this connection also it may be stated that the analyst's work belongs to a number of mass phenomena which can be subjected to statistical investigations.

In so far as the result of every analytical determination can be considered as the sum of a large number of mutually independent items: operations of weighing, measuring volumes, precipitations, filtrations, etc., each of which is subject to the effect of multiform conditions, it is usually possible to assume that the random errors of all normal chemical methods of analysis obey the law of normal distribution:

$$f(x,\sigma) = \frac{1}{\sigma\sqrt{2\pi}}\, e^{-\frac{(x-a)^2}{2\sigma^2}}, \qquad (1)$$

where a is the true value of the quantity determined, x – the value obtained by a given measurement, e – the base of the natural logarithms and σ^2 – the variance which is equal to the sum of the squares of the deviations of the observations from their mean divided by the number of observations, calculated according to the formula:

$$\sigma^2 = \frac{(x_1-\bar{x})^2+(x_2-\bar{x})^2+\cdots+(x_n-\bar{x})^2}{n} = \frac{\sum_{i=1}^{n}(x_i-x)^2}{n}. \qquad (2)$$

The square root of this quantity is called the mean square deviation of an

individual result from the arithmetic mean or the standard deviation.

In formula (2) n is the number of measurements made in order to determine the arithmetic mean x, which in turn is calculated from the formula

$$\bar{x} = \frac{x_1 + x_2 + \ldots + x_n}{n} = \frac{\sum_{i=1}^{n} x_i}{n}. \quad (3)$$

By means of the equation expressing the law of normal distribution (1) it is possible to calculate the probability of the occurrence of an error in measurement $x - a$, if a and σ^2 are known. For practical purposes however it is much more important to have a sufficiently reliable evaluation of the probability that in any determination of a quantity a, the deviation of a random result x, i.e., the value of $x - a$ does not exceed some given value t. The respective values of the probability $P_{0,t}$ that the error does not exceed the limits [0, t] are calculated by means of the probability integral:

$$\Phi(z) = \frac{1}{\sqrt{2\pi}} \int_0^z e^{-t^2} 2\,dt = P_{0,t}\,, \quad (4)$$

which as Equation (4) shows is a function of its upper limit z. Tables for the probability integral written in formula (4) can be found in textbooks on the theory of probability [1,2]. In using such tables $z = t/\sigma$ is taken as the argument, where t is the limit of the interval and σ is the mean square deviation of the result. Similar tables in some textbooks on mathematical statistics [3,4] are compiled for the double interval $[-t,t]$ and differ from (4) by the factor 2; when $z = t/\sigma$ is substituted, the value of $\Phi(z)$ given in such tables gives $P_{-t,t}$ the probability of a random error $x - a$ occurring in the interval $[-t,t]$. The same probability is given by tables [5,6,7,8] for the function

$$\Phi(z) = \frac{2}{\sqrt{\pi}} e^{-t^2} dt = P_{-t,t}\,, \quad (5)$$

the argument of which is the quantity $z = \frac{t}{\sigma\sqrt{2}}$.

As the tables show, the value of the probability integral expressed by formula (4) tends to 0.5 as z increases, while for the remaining formulas it tends to unity.

Already for $t = 3\sigma$ the value of $P = \Phi(3) = 0.997$ shows that 997 measurements in every 1000 give results which do not overlap the limits $[a - 3\sigma, a + 3\sigma]$. It is because of this that σ^2 plays such an important part as the characteristic of scattering, while the "three sigmas" rule is constantly used in practice because it enables the interval to be determined within the limits of which it is possible to get the true value of the quantity being determined with a probability (reliability) approaching unity.

Unfortunately all the formulas adduced above include the true value of the quantity being determined and they are deduced on the assumption that the number of measurements made is so large that the distribution curve (1) is continuous. In actual analytical practice the number of measurements made is very small and the true value a is the value sought, and must be determined in spite of the large gaps in the series of measurements.

Under these conditions all the purport of the application of the theory of errors to cases of analysis involving only a small number of individual measurements is based on the following ideas:

Let us assume that in all, three measurements of a given quantity have been made and that the results obtained do not differ widely. It is evident that such a coincidence can occur even in the two following extreme cases.

1. All three measurements simultaneously include coarse errors which occur as the result of elementary errors acting on the three results in the same direction.

2. All three results belong to the most probable groups of results i.e., include only small errors.

The probability of the first case is very small, since the probability of a result with a large random error is very small, so that the probability of all three results including large errors is equal to the product of three such low probabilities, i.e. the final probability is also very low.

The probability of the second case is very much higher since it is equal to the probability of getting the most frequent result sufficiently close to the quantity to be determined, a.

An approach of this type to an explanation of the convergence of the results of a comparatively small number of measurements leads to the important conclusion that the most probable result for any group of independent measurements is the arithmetic mean $\bar{x}$ calculated by formula (3) since the sum of the squares of the deviation of the results of separate measurements from their arithmetic mean has a minimum value.

This means that it is precisely by such a choice of the most probable value of the determined quantity that the deviation of $x_i - \bar{x}$ approaches most closely to the ideal distribution curve.

It was found that the arithemtic mean in the general case is not equal to the exact value of a, since

$$\bar{x} = a - \frac{\sum_{i=1}^{n} u_i}{n} , \tag{6}$$

where $u_i = x_i - a$, i.e. represents the true error of the measurement. From equation (6) it follows that $\bar{x} \longrightarrow a$ the greater the number of measurements n, and the equation $\bar{x} = a$ is realized only at $n = \infty$ It appears that the real true errors are distributed by the normal law, and their variance σ_u^2 can be calculated according to the formula:

$$\sigma_u^2 = \sigma^2 \frac{n}{n-1} = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1} . \tag{7}$$

The square root of this quantity, viz, σ_u, is called the mean square error of an individual determination.

It has been established moreover that the variance of the mean square $\sigma^2_{\bar{x}}$ is n times less than the variance of the true error σ_u^2 which means that

$$\sigma^2_{\bar{x}} = \frac{\sigma_u^2}{n} = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n(n-1)} \tag{8}$$

The square root of this quantity is called the mean square error of the mean value.

These formulas are of immense significance since they give the value of σ by means of which it is possible to find the argument of the probability integral $\Phi(z)$ and to determine with a given probability the limits within which a lies. Nevertheless the direct use of function $\Phi(z)$ is only possible if the number of individual measurements n is so large that the values of σ^2 found in this way are practically the same as σ^2 for $n = \infty$, which is called the variance of the general aggregate, in contrast to the so-called estimate of variance s^2, calculated by the same formula for any values of n.

In so far as $\bar{x}$ and s^2 are determined directly from experimental results it is to be expected that a method can be found for the determination of the sought for value of a by means of their values for any n. This problem is one of the three fundamental problems of mathematical statistics which can be formulated as follows.

1. The value of σ^2 is known and it is necessary to evaluate the unknown value of $\underline{a}$, i.e. to find $\underline{a}$, the values of $[\beta_1, \beta_2]$ (confidence limits) between which the true value of $\underline{a}$ is to be found and the reliability α, i.e., the probability that the true value a lies in the interval $[\beta_1, \beta_2]$.

2. The value of $\underline{a}$ is known and σ^2 remains to be determined.

3. Both $\underline{a}$ and σ^2 remain to be determined.

All these problems have been solved since it was successfully shown that for cases where the distribution of $\underline{x}$ in the general aggregate is normal and has a mean $\underline{a}$, the distribution of the quantity

$$t_1 = \frac{|\bar{x} - a|}{s_{\bar{x}}} \tag{9}$$

for any $\underline{n}$ follows Student's law exactly. According to this law the probability of the value of the quantity t_1 lying between t_1 and $t_1 + dt$, is expressed by the formula

$$P_{t_1, t_1+dt} = c \left(1 + \frac{t_1^2}{k}\right)^{-\frac{k+1}{2}} dt, \tag{10}$$

where $\underline{c}$ is a constant and $\underline{k} = \underline{n} - 1$ is the so called number of degrees of freedom.

Special probability tables have been compiled $P(|t|) \geqslant t_1)$ according to Student's distribution [9] in which are given the probabilities for values of $\underline{t}$ which are not less in numerical value than a given number, if $\underline{x}$ and $\underline{s_{\bar{x}}}$ are determined for an amplitude $\underline{n}$, i.e. on the basis of the results of $\underline{n}$ individual independent measurements; $x_1, x_2, \ldots, x_n$ that correspond to $\underline{k} = \underline{n} - 1$ degrees of freedom.

Like all other distributions used in mathematical statistics, the $\underline{t}$ distribution assumes only random deviations $x_i - \bar{x}$. Thus for $t_1 = 4.5$ at $\underline{k} = 5$ we find in the table a probability of 0.006, that is usually written in the form $P(|t| \geqslant 4.5) = 0.006$ or $P(-4.5 < t_1 < 4.5) = 1 - 0.006 = 0.994$. This result can be interpreted as follows; it expresses the probability that the function t_1 for $\underline{k} = 5$ is either equal to or greater than 4.5 as a result of the occurence of only random errors in the measurements $x_1, x_2, \ldots, x_n$ is equal to 0.006, i.e., it is very small. This enables us to conclude that t_1 attains the value of 4.5 not accidentally but as the result of some systematic deviation of the value x_i, i.e. of $\bar{x}$ from $\underline{a}$.

The same table can also be used for evaluating the interval $[\beta_1, \beta_2]$ within the limits of which the true value of the determined quantity α lies with a probability of $\underline{a}$. If it is arranged that the probability $\alpha = 0.95$ for $\underline{k} = 8$ then it is necessary to find t_1 from the table for which $P(|t| \geqslant t_1) = 1 - 0.95 = 0.05$ (in the given case $t_1 = 2.3$). Substituting this value in formula (9) it follows that

$$a = \bar{x} \pm t_\alpha s_{\bar{x}} = \bar{x} \pm \epsilon_\alpha. \tag{11}$$

Here α is the reliability, $\epsilon_\alpha = t_\alpha s_{\bar{x}}$ the accuracy of the approximation equation $\bar{x} \approx a$ and $[\bar{x} - \epsilon_\alpha, \bar{x} + \epsilon_\alpha]$ the confidence limits for the value.

It is obvious that (11) replaces the "three sigmas" rule for analyses involving only a small number of samples ($n \geqslant 2$).

Special tables [10,11,12] exist for the determination of values of t_α for values α equal to 0.90, 0.95, 0.98, 0.99 and 0.999 and different values of $\underline{k} = \underline{n} - 1$. By means of these tables, knowing $\underline{k}$ and assigning a definite value of α, the value of $\underline{t_\alpha}$ which enters into formula (11) can be found directly.

Cases are often observed where the analytical results of the same sample

carried out by two different laboratories, or in the same laboratory by different operators, or by different methods, or simply at different times are characterized by different variances.

In such cases the question arises as to whether the variances differ in a random manner or whether the variances can be traced to serious causes such as poor organization in the laboratory where the variances are highest, or poor reproducibility of results obtained by one of the methods, or differences in operating techniques, or appreciable changes in the quality of the work at different stages of an analytical process.

In cases of this type the ratio of the estimates of variance is used for comparison

$$T_H = \frac{s_1^2}{s_2^2}, \qquad (12)$$

in the numerator of which the greater estimate of variance s_1^2 or s_2^2 calculated by formula (7) is always placed. The value of T_H is greater the greater the divergence of the estimates of variance. Let us assume that our s_1^2 and s_2^2 are variances of a random choice, belonging to one Universe. In this case the differences between them can be explained only by the fact that for the determination of s_1^2 and s_2^2 only a limited number of measurements were made, say n_1 and n_2. It is evident that as n_2 and n_1 increase both estimates of variance will tend to the same value σ^2 and their ratio T_H to unity. For a limited number of measurements the value of T_H can deviate from unity as a result of random variations, and is greater the less n_1 and n_2, which means k_1 and k_2. As a result of the investigation of the T distribution special tables have been compiled. There are two such tables in V.I.Romanovsky's book [13]. They both include values of T which can occur as the result of random causes, if s_1^2 is obtained for k_1 and s_2^2 for k_2 degrees of freedom. The first of these tables contains values of T_5 calculated with a probability of 0.05, while the second T_1 is calculated on a probability of 0.01.

In Dlin's book [14], in one of the tables in addition, for different k_1 and k_2, values are adduced for P = 0.05, P = 0.01 and P = 0.001. It is clear that the estimates of variance s_1^2 and s_2^2 for which $T > T_5$ besides T_1 and T_{01} (P = 0.001) cannot be ascribed to random divergence. In such cases it can be stated that there is a serious reason for this divergence which is the result, e.g., of an incorrect approach to the problem, poor reproducibility of one of the methods etc..

If, e.g., s_1^2 and s_2^2 are estimates of variance for the same analytical method which are obtained at different times in the same laboratory and $s_1^2 \gg s_2^2$, this fact signalizes the breakdown of normal working procedure. In this case it must be remembered that the variance of any method σ^2 is an additive quantity.

$$\sigma^2 = \sigma_\alpha^2 + \sigma_\beta^2 + \ldots + \sigma_\omega^2, \qquad (13)$$

where σ_ν^2 is the variance of individual operations (e.g. weighing etc.). This means that in order to restore normal work it is necessary to explain which of these σ_ν^2 is responsible for the divergence and to eliminate it by controlling the corresponding process.

Finally in a number of cases, the analyst must assess the variance of the method which can be evaluated as the variance of the Universe σ^2, from the results of a small number of analyses n which only enables the estimate of variance s^2 to be calculated. This problem can be solved with a sufficient degree of approximation by means of the inequality

$$s - \frac{3s}{\sqrt{2(n-1)}} < \sigma < s + \frac{3s}{\sqrt{2(n-1)}}, \qquad (14)$$

which determines the confidence limits of the required variance of the method.

The inequality (14) is compiled according to the "three sigmas" rule because the mean square deviation for the mean square deviation itself, i.e. s_s, can be determined sufficiently accurately by means of the formula

$$s_s = \frac{s}{\sqrt{2(n-1)}} \tag{15}$$

It very often happens that in the investigation of new standard samples the work is entrusted to a few analysts or laboratory assistants each of whom gives a series of values for the quantities being determined and the respective arithmetic mean, and variance. If subsequent analysis of these results show that the deviation between individual means and variances can be related to random errors, then the new, corrected value of the mean is calculated by the formula:

$$\bar{x} = \frac{n_1\bar{x}_1 + n_2\bar{x}_2 + \ldots + n_p\bar{x}_p}{n_1 + n_2 + \ldots n_p} = \frac{\sum_{\alpha=1}^{p} n_\alpha \bar{x}_\alpha}{\sum_{\alpha=1}^{p} n_\alpha}, \tag{16}$$

where $\bar{x}_1$ is the mean in the first series of measurements with amplitude n_1, etc..

If further for the same p series of measurements, the amplitudes of which are respectively equal to $n_1, n_2, \ldots, n_p$, the means found $\bar{x}_1, \bar{x}_2, \ldots, \bar{x}_p$ and the estimates of variance $s_1^2, s_2^2, \ldots, s_p^2$, then for the whole aggregate of $n_1+n_2 \ldots + n_p = \Sigma n_\alpha$, the measurements of the estimates of variance s^2 are determined by the formula;

$$s^2 = \frac{n_1 s_1^2 + n_2 s_2^2 + \ldots + n_p s_p^2}{\sum n_\alpha} + \frac{n_1(\bar{x}_1 - \bar{x})^2 + n_2(\bar{x}_2 - \bar{x})^2 + \ldots + n_p(x_p - x)^2}{\sum n_\alpha}$$

or

$$s^2 = \frac{\sum_{\alpha=1}^{p} n_\alpha s_\alpha^2}{\sum_{\alpha=1}^{p} n_\alpha} + \frac{\sum_{\alpha=1}^{p} n_\alpha (\bar{x}_\alpha - \bar{x})^2}{\sum_{\alpha=1}^{p} n_\alpha}, \tag{17}$$

where $\bar{x}$ is determined by formula (16).

The information given above is sufficient for consciously using the methods of mathematical statistics for normal analytical work. These methods are illustrated below by a number of examples taken from analytical practice. Special formulas which are often used for similar purposes [15,16] are obtained on the basis of the same fundamental considerations outlined above.

Calculations which must be used to carry out a statistical treatment of analytical results reduce to a determination of the arithmetic mean and the variance. The arithmetical calculating part of the work can be simplified considerably by means of the following formulas:

$$\bar{x} = c + \frac{\sum_{i=1}^{n} (x_i - c)}{n}, \tag{18}$$

$$\sum_{i=1}^{n} (x_i - \bar{x})^2 = \sum_{i=1}^{n} (x_i - c)^2 - n(c - \bar{x})^2, \tag{19}$$

$$\sum_{i=1}^{n} (x_i - \bar{x})^2 = \sum_{i=1}^{n} x_i^2 - \frac{\left(\sum_{i=1}^{n} x_i\right)^2}{n} \tag{20}$$

In formulas (18) and (19), $\underline{c}$ is any number, but it is convenient to choose it so that it does not differ very much from the actual arithmetic mean and is also convenient for calculating the differences $x_i - c$. When using formulas (18) and (19) for numbers on which it is necessary to operate, the number of signs can be reduced considerably; subsequent determination of the differences in squares can be done mentally or with the help of a small table of squares.

Formula (20) is suitable in those cases where the original x_i includes a small number of signs; otherwise Barlow's tables must be used.

Present day analysts in whatever laboratories they work often have to solve the following problems.

1) To choose the best of two published methods for determining the same thing.

2) To use a chosen analytical method, i.e., to find the amount of some compound in a test sample with a fair degree of accuracy and to evaluate this approximation, having eliminated spurious results.

3) To analyze the results obtained in order to explain their stability to random effects and to eliminate possible systematic errors.

4) To present the results obtained in such a form that anybody entrusted to carry out a similar analysis gets not only the figures characterizing the percentage of compound to be determined in a sample but also an exact idea of the reliability of the result.

Analysts concerned with developing new methods should in this connection give all the results in their articles so that any chemist can use the new method in the most rational manner.

Every article should therefore contain:

1) a detailed description of all the precautions and apparatus which the author of the article used so as to show that the recommended method does not include systematic errors.

2) information on results obtained by means of the new method for varying initial concentrations of the test compound.

3) results characterizing the systematic errors of the method in the presence of other materials.

Every investigation of this type includes a number of separate analyses and measurements, but no journal is prepared to publish all the results. In this connection therefore authors usually publish only an insignificant amount of all their numerical data, which in their opinion is sufficient to evaluate the method, and leave out as a consequence a number of results which lower the value of a particular piece of work.

By adopting a statistical treatment of the results of such research work, all the material accumulated can be made accessible to the reader in the form of a few figures which characterize:

1) the value of $\underline{n}$ (the number of anlyses) or $\underline{k} = \underline{n} - 1$,

2) the value of the estimate of variance s^2 or the variance σ^2;

3) the value of the accuracy $\epsilon_\alpha = t_\alpha s_{\bar{x}}$ with an indication of the probability adopted α;

4) the confidence limits which determine the systematic errors;

5) the relation between the variance of the method and the initial concentration of the test compound;

6) the relation between the variance of the method and the concentration

of any other ions in the system.

Such an approach to formulating the work done facilitates the introduction of new analytical methods, since the practising analyst having read the article will be in possession of all the results characterizing the method.

At the same time the feeling of responsibility on the part of the author increases since the statistical characteristics $\bar{x}$ and σ^2 are much more reliable than the individual measurements hitherto published and should be capable of being repeated by anyone.

Information about standard samples should also contain the accuracy of each $\epsilon_\alpha = t_\alpha s_{\bar{x}}$ with an indication of the reliability and also the values of $k = n - 1$ and s^2, since in the absence of these results, a decision on the question of the "non-coincidence of results with the normal" becomes impossible.

The examples quoted below are taken from Russian chemical journals, major attention being given to the question of evaluating a new method and comparisons of the various methods.

A. A General Evaluation of a Method from the Results Obtained by Using it for Samples whose Compositions are Already Known

In Zolotukhin's paper [18] results are given for four acidimetric determinations of beryllium in a test containing 2.655 mg equivalents of $BeSO_4$. In table 1 these results are treated statistically, it being assumed that the initial value of 2.655 mg equivs. does not contain any errors although there is no proof of this in Zolotukhin's article. Calculations of $\bar{x}$ are carried out by means of (18), of $\Sigma(\bar{x}_1 - \bar{x})^2$ by (19) and finally the divergence between $a = 2.655$ and $\bar{x} = 2.6465$ mg equivs. is investigated by means of formulas (9) and (11) and Student's tables of distribution [9].

From table 1, $t_1 = 3.27$ for $k = 4 - 1 = 3$. In the probability tables $P(|t| \geqslant t_1)$ calculated according to Student [9] we find that $P(|t| \geqslant 3.2) = 0.048$ and $P(|t| \geqslant 3.3) = 0.045$. Simple interpolation gives $P(|t| \geqslant 3.27) = 0.046$. This result is used as follows.

1. The value of t_1 is found from formula (9), assuming that the deviation between the value of a and $\bar{x}$ depends on various random causes.

2. It was found that $t_1 = 3.27$ and that the probability of the occurence of a value of $t \geqslant 3.27$ for $k = 3$ is equal to 0.046.

3. If it is arbitrarily agreed to split up all the values of t_1 which occur only as a result of random causes into those of low probability, i.e., those rarely met, and those which turn up pretty often, and to relate to the low probability group all those t_1's for which $P(|t| \geqslant t_1) < 0.05$, then it must be accepted that the value of $t_1 = 3.27$ has occured as the result of systematic errors.

TABLE 1

Investigation of the results of acidimetric determination of $BeSO_4$ by V.K.Zolotukhin's method
$a = 2.655$ mg equiv. $BeSO_4$

No.	$BeSO_4$ found x_i mg. equiv.	$(x_i - 2.645) \cdot 10^3$	$(x_i - 2.645)^2 \cdot 10^6$
1	2.649	4	16
2	2.640	-5	25
3	2.645	0	0
4	2.652	7	49
Total		$6 \cdot 10^{-3}$	$90 \cdot 10^{-6}$

$$\bar{x} = 2.645 + \frac{6\cdot10^{-3}}{4} = 2.645 + 1.5\cdot10^{-3} = 2.6465;$$

$$\sum_{i=1}^{4} (x_i - \bar{x})^2 = 90\cdot10^{-6} - 4(1.5\cdot10^{-3})^2 = 81\cdot10^{-6};\ s^3 = \frac{81\cdot10^{-6}}{4-1} = 27\cdot10^{-6};$$

$$s_x = \sqrt{\frac{81\cdot10^{-6}}{4(4-1)}} = 2.6\cdot10^{-3};\ t_1 = \frac{|2.655 - 2.6465|}{2.6\cdot10^{-3}} = \frac{8.5\cdot10^{-3}}{2.6\cdot10^{-3}} = 3.27$$

4. In order to evaluate the systematic errors, the value of $t_{0.95}$ for $k = 3$ is found and substituted in the formula (9); from this it follows that $\bar{x} - a = \pm 3.16 \cdot 2.6\cdot10^{-3} = \pm 8.2\cdot10^{-3}$.

5. It is obvious that the systematic error $E = \bar{x} - a$ is evaluated with the same accuracy $\pm 8.2\cdot10^{-3}$, i.e., that with a reliability of 0.95 it can be asserted that E is included in the interval $[8.5\cdot10^{-3} - 8.2\cdot10^{-3},\ 8.5\cdot10^{-3} + 8.2\cdot10^{-3}]$ or $[3\cdot10^{-4},\ 1.7\cdot10^{-2}]$. This interval is very big but by increasing the number of titrations it should be possible to decrease it. We do not know how many measurements V.K.Zolotukhin made; one thing is however, clear, viz., the results given in the article are insufficient to form a judgement of the method.

If Zolotukhin had treated his results statistically then for any number of experiments n he could have characterized his results in one line instead of in a whole table. All he would have had to write would be the values of a, n, $\bar{x}$, s^2, $s_{\bar{x}}$, t_1, $P(|t| \geqslant t_1)$, t_α, $t_\alpha s_{\bar{x}}$ and $E = a - \bar{x}$.

An analyst reading the article containing this information would get a complete picture of the method and could evaluate $s_{\bar{x}} = \frac{s}{\sqrt{n}}$ in particular for any number of tests n, i.e. the relative probable error of the method

$$\pm \frac{t_\alpha s_{\bar{x}} \cdot 100}{\alpha \sqrt{n}}, \qquad (21)$$

B. Evaluation of the Effect of Other Components

In Naumov's paper [19] the effect of ethylene oxide on the optical density (D) of m-phenylendiamine in its mixtures with acetaldehyde was investigated. In Table 2 results of the statistical treatment of the results from Table 3 of Naumov's paper are given. In this case instead of $\bar{x}$ and the value of a, which is regarded as reliable, it is necessary to compare the mean values of the two series of experiments, i.e. the values of $\bar{x}_1$ and $\bar{x}_2$. For this purpose the following formulas are used:

$$t = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{\bar{x}}}, \qquad (22)$$

$$s_{\bar{x}} = s\sqrt{\frac{n_1 + n_2}{n_1 n_2}}, \qquad (23)$$

$$s = \sqrt{\frac{\sum_{i=1}^{n_1} (x_{1i} - \bar{x}_1)^2 + \sum_{j=1}^{n_2} (x_{2j} - \bar{x}_2)^2}{n_1 + n_2 - 2}}, \qquad (24)$$

$$k = n_1 + n_2 - 2, \qquad (25)$$

TABLE 2

The effect of ethylene oxide on the optical density (D) of m-phenylendiamine in its mixtures with acetaldehyde.

No.	CH_3CHO in %	$(CH_2)_2O$ in %	D_i	$(D_i - \bar{D}) \cdot 10^2$	$(D_i - \bar{D})^2 \cdot 10^4$	s^2	$\bar{D}_s$
1	0.051	0.00	1.22	2	4		
2	0.051	0.00	1.17	-3	9		
3	0.051	0.00	1.18	-2	4		
4	0.051	0.00	1.23	3	9		
		$\bar{D}_1$	=1.20		$26 \cdot 10^{-4}$	$8.7 \cdot 10^{-4}$	$1.48 \cdot 10^{-2}$
1	0.051	1.50	1.26	2	4		
2	0.051	1.50	1.22	-2	4		
		$\bar{D}_2$	=1.24		$8 \cdot 10^{-4}$	$8 \cdot 10^{-4}$	$2.00 \cdot 10^{-2}$
1	0.051	2.35	1.28	-0.5	0.25		
2	0.051	2.25	1.29	0.5	0.25		
		$\bar{D}_3$	=1.285		$0.5 \cdot 10^{-4}$	$0.5 \cdot 10^{-4}$	$5.00 \cdot 10^{-3}$
1	0.051	4.50	1.34	-3	9		
2	0.051	4.50	1.40	3	9		
3	0.051	4.50	1.37	0	0		
		$\bar{D}_4$	=1.37		$18 \cdot 10^{-4}$	$9 \cdot 10^{-4}$	$1.73 \cdot 10^{-4}$

where $\bar{x}_1$ is the mean for the first series of analyses, etc., and x_{1i} the individual results of the first series of analyses etc

1. First the compatibility of the results of all four series must be tested. In order to do this it is sufficient to compare the extreme values of s^2: $s_4^2 = 9 \cdot 10^{-4}$ and $s_3^2 = 0.5 \cdot 10^{-4}$ for $k_4 = 2$ and $k_3 = 1$. Using formula (12) and the table of T distributions [13] we find that $T_H = s_4^2/s_3^2 = 18$ is much smaller than the tabular value of T for the same k, which is equal to 199.5. It is obvious that the greatest divergence in the variances between individual series of Naumov's results are completely explained by random errors.

2. Using formulas (24), (23), and (22) for the first two series of experiments we get $s = 2.92 \cdot 10^{-2}$, $s_{\bar{D}} = 2.53 \cdot 10^{-2}$, $\bar{D}_1 = 1.20$, $\bar{D}_2 = 1.24$, $t_1 = 1.59$. Further in the Student's tables of [9] distribution we find that for $k = 4 + 2 - 2 = 4$ $P(|t| \geqslant 1.6) = 0.185$. This means that the probability of the occurence of a value $t = 1.59$, only as a result of random errors is so great that it is impossible to ascribe the small increase in $\bar{D}_2$ to the presence of 1.5% ethylene oxide.

3. A similar treatment of the results of the first and third series leads to the following values: $k = 4$, $s = 2.58 \cdot 10^{-2}$, $s_{\bar{D}} = 2.23 \cdot 10^{-2}$ $[\bar{D}_1 - \bar{D}_3] = 8.5 \cdot 10^{-2}$, $t_1 = 3.82$ and $P(|t| \geqslant 3.82) = 0.019$. The probability found is less than 0.05; it is impossible therefore to attribute the value of $t_1 = 3.82$ to random errors, and it must be accepted that systematic changes occur in the optical density as a result of the presence of ethylene oxide.

In order to evaluate the confidence limits we find t_α by the tables [10,11,12], for $k = 4$ $t_{0.95} = 2.78$; then $\epsilon_{0.95} = \pm 2.78 \cdot 2.23 \cdot 10^{-2} = \pm 6.2 \cdot 10^{-2}$, and the confidence limits are respectively equal to $8.5 \cdot 10^{-2} - 6.2 \cdot 10^{-2} = 2.3 \cdot 10^{-2}$ and $8.5 \cdot 10^{-2} + 6.2 \cdot 10^{-2} = 14.7 \cdot 10^{-2}$.

4. Finally a comparison of the first and fourth series gives $k = 5$, $s = 2.97 \cdot 10^{-3}$, $s_{\bar{D}} = 2.27 \cdot 10^{-2}$, $|\bar{D}_1 - \bar{D}_4| = 0.17$, $t_1 = 7.5$ $P(|t| \geqslant 6.0) = 0.002$ and consequently, $P(|t| \geqslant 7.5 < 0.002$, which means that $t_1 = 7.5$ is not accidental. Further for $k = 5$ $t_{0.95} = 2.57$, $\epsilon_{0.95} = \pm 5.8 \cdot 10^{-2}$ and the confidence limits for the value

$E = \bar{D}_1 - \bar{D}_4$ have the values 0.11 and 0.23.

By comparing the limits found $[2.3 \cdot 10^{-2}, 14.7 \cdot 10^{-2}]$ and [0.11, 0.23], it can be affirmed that Naumov should have plotted sections of straight lines in 0.12 units of optical density, instead of points on his graph No. 3.

It is highly possible that Naumov made a far greater number of measurements, since a measurement of D does not require much time, but he has not included these in his article and as a result of reading his paper a number of doubts and questions arise. At the same time by adopting a statistical method of treating the results, he could have represented all his results in the form of one table compiled as follows:

CH_3CHO, %	$(CH_2)_2O$, %	n	$\bar{D}$	$\sum(D_i - \bar{D})^3$	s^2	$s_{\bar{D}}$
---	---	---	---	---	---	---
---	---	---	---	---	---	---
---	---	---	---	---	---	---

All Naumov's results occupying 11 lines in his paper can be written in four lines.

C. Evaluation of a Method by Comparing the Results Obtained by this Method in the Determination of Various Amounts of a Test Compound, With those of Similar Determinations Carried out by Means of a Standard Method.

This type of experiment is often met. When it is used it is assumed that the results x_i obtained by a standard procedure is free from errors. The results y_i obtained by the test method can include errors, and the problem reduces to a determination of random variations during repeated determinations y.

In the articles describing such methods, two series of parallel results, those for x_i and y_i, are given, which cover the concentration range in which the author is interested. Direct statistical treatment of such results is impossible, and therefore an investigation of the ratio y_i/x_i is made instead, since these should maintain their value from one experiment to another.

1. In Table 3, columns 2 and 3, results are adduced from Table 4 of Golubtsova's article [20], which show that the hydrolytic separation of Nb from mineral acid solutions gives the same results as from $HClO_4$ solution. Here x_i are the values obtained with $HClO_4$ which must be regarded as free from errors and y_i are the parallel values for mineral acid media. The values of $z_i = y_i/x_i$, as can be seen from the table, vary around 1.003 and $s = 7.1 \cdot 10^{-4}$ is the practical estimate of variance of y_i since all the values of y_i/x_i lead to $x_i = 1\%$.

An analyst following Golubtsova's method can use the value s^2 as follows. Let us assume that three determinations of Nb were made and that an average content of 2.72% of this element was found. Then $s_{\bar{y}} = s/\sqrt{3}$ and for $k = 2t_{0.95} = 4.30$, which means that the accuracy $\epsilon_{0.95} = \pm t_{0.95} \cdot s_{\bar{y}} = 4.30 \cdot 2.7 \cdot 10^{-2}/\sqrt{3} = 6.7 \cdot 10^{-2}$ %, from which the relative error should not, for a probability of 0.95, exceed in a given analysis $6.7 \cdot 10^{-2} \cdot 10^2/2.72 = 2.5\%$.

The question as to whether the test method includes systematic errors or not must be solved in a more complicated manner [21].

1. The constants a and b of the linear equation $Y = a + bx$, connecting the values of x regarded free from errors with the values which might contain errors Y, are determined in the usual way.

TABLE 3

Results of the hydrolytic separation of Nb in the presence of $HClO_4$ (x_i) and in mineral acid media (y_i)

No.	Nb found in Percent		$\frac{y_i}{x_i} = Z_i$	$(Z_i - \bar{Z}) \cdot 10^3$	$(Z_i - \bar{Z})^2 \cdot 10^6$
	x_i	y_i			
1	3.14	3.19	1.0160	+13	169
2	2.63	2.59	0.9846	-18.4	338.56
3	1.26	1.22	0.9682	-34.8	1211.04
4	1.09	1.11	1.0190	+16	256
5	1.06	1.04	0.9810	-22	484
6	0.58	0.60	1.0350	+32	1024
7	0.39	0.38	0.9742	-28.8	829.44
8	0.18	0.19	0.0555	+52.5	2756.25
9	0.17	0.17	1.0000	-0.3	0.09
10	0.16	0.16	1.0000	-0.3	0.09
11	0.08	0.08	1.0000	-0.3	0.09
Total	10.74	10.73	11.0335		$7,069 \cdot 10^{-3}$
Mean	0.9766	0.9754	1.0030		

$$s^2 = \frac{7.0691 \cdot 10^{-3}}{10} = 7.1 \cdot 10^{-4}; \quad s = 2.7 \cdot 10^{-2}$$

TABLE 4

Results of the conductometric titration of zinc acetate ($ZnAc_2$) with barium hydroxide

No.	$ZnAc_2$ taken, in mg, x_i	$ZnAc_2$ found, in mg, y_i	$\frac{y_i}{x_i} = Z_i$	$(Z_i - \bar{Z}) \cdot 10^4$	$(Z_i - \bar{Z})^2 \cdot 10^8$	X, in mg
1	16.63	16.63	1.0000	-163	26569	16.63
2	11.09	11.12	1.0033	-130	16900	11.09
3	5.54	5.58	1.0075	-88	7744	5.52
4	1.85	1.95	1.0543	380	144400	1.86
Total	35.11	35.28	4.0651		$1,956 \cdot 10^{-3}$	
Mean			1.0163			

$$s^2 = 6.5 \cdot 10^{-4}$$

2. $\sum (y_i - Y_i)^2$ is found and then the estimates of variances s_y, s_a, s_b determined by means of the formulas

$$s_y^2 = \frac{\sum_{i=1}^{n} (y_i - Y_i)^2}{n - 2}, \quad s_a^2 = s^2 \frac{\sum_{i=1}^{n} x_i^2}{n \sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2}, \quad s_b^2 = \frac{s^2}{\sum_{i=1}^{n} x_i^2 - \bar{x} \sum_{i=1}^{n} x_i}, \quad (26)$$

where s_y^2 is the estimate of variance of an individual analysis, s_a^2 the estimate of variance of $\underline{a}$ and s_b^2 the estimate of variance of $\underline{b}$.

3. The value of $t_a = \frac{|a|}{s_a}$ and its probability for $k = n - 2$ are found from a Student's distribution table [9]. If when this has been done it appears that the occurence of values of t_a as a result of only random errors has a low probability, then it may be accepted that the method includes a systematic error t_a,

the confidence limits of which are determined by formula (11) for $\underline{k} = \underline{n} - 2$, with the help of values of t_a, which are found in special tables [10,11,12].

4. The compatibility of the variances obtained directly and indirectly by investigating the ratio $y_i/x_i = z_i$, since for a case of large divergence, it is to be expected that the value of the variance, will change with the concentration of the test material.

5. Finally the average value of $\overline{y_i/x_i} = \bar{z}$ is compared with the value of the tangent of the straight line $\underline{b}$.

All this work should of course be carried out when the method is tested, but usually authors of new analytical procedures publish only some of their results, presuming apparently that every analyst can get all the characteristics which he needs independently. Golubtsova did not carry out such a statistical treatment. Our calculations show that in this case $\underline{Y} = -0.0028 + 1.002x$, while $s_y^2 = 7.9 \cdot 10^{-4}$, $s_b = 8.6 \cdot 10^{-3}$, $s_a = 1.2 \cdot 10^{-2}$ as a result $t_a = 0.24$. In so far as $P(|t| \geqslant 0.24 = 0.846$, if $\underline{k} = 9$, then it can be stated that $\underline{a} = -0.0028$ is the result of random errors and this means that the straight line should go through the origin. At the same time the value for $b = 1.002$ which is in good agreement with $\bar{z} = 1.003$ s_y^2 with a value of s^2 is derived in Table 3.

All these results show that the hydrolytic precipitation of Nb in mineral acids does not differ in practice from precipitation from $HClO_4$ solutions.

As the second example of this type we shall use the results of Udovenko and Pasovskaya [22] on the conductometric titration of zinc acetate with barium hydroxide. The results for the statistical treatment of the experimental data are given in Table 4.

In this case according to Table 4, $s^2 = 6.52 \cdot 10^{-4}$, while the estimate of variance and the mean square error calculated by formula (24) have the values $s_y^2 = 4 \cdot 10^{-4}$, $s_a = 1.86 \cdot 10^{-2}$ and $s_b = 1.8 \cdot 10^{-3}$. The equation for the straight line in this case is of the form $\underline{Y} = -0.0952 + 0.9940x$, while $t_a = \frac{9.5 \cdot 10^{-2}}{1.86 \cdot 10^{-4}} \approx 5.12$, and for $k = 4 - 2 = 2P(|t| \geqslant 5.0) = 0.038$, the value of $t_a = 5.12$ cannot therefore be attributed to random errors. By rewriting the equation of the straight line in the form $X = -0.0958 + 1.006y$, it can be used for calculating the required values of $\underline{X}$ which are given in the last column of Table 4.

It is evident that this method gives satisfactory results. It is necessary to note in particular that the estimate of variance $s^2 = 6.5 \cdot 10^{-4}$ calculated from the results of Table 4 differs only very slightly from the estimate of variance $s_y^2 = 4 \cdot 10^{-4}$, calculated by means of formulas (26). This fact shows that in the conductometric determination of ZnAc the variance of the method is practically independent of the amount of test material.

As a third example we shall quote Udovenko's and Pasovskaya's results [23] on the conductometric determination of KCl with sodium picrate. The statistical treatment is given in Table 5.

In this case according to the results in Table 5, $s^2 = 1.22 \cdot 10^{-4}$; the equation for the straight line $\underline{Y} = -2.41 + 1.028x$; calculations by formula (26) give; $s_y^2 = 0.606$; $s_a = 1.15$; $s_b = 1.1 \cdot 10^{-2}$ and $t_a = 2.09$. According to Student's tables of distribution [9] for $\underline{k} = 3$ $P(|t| \geqslant 2.1) = 0.127$. Although this value is small it is still greater than 0.05 which we have hitherto regarded as a provisional limit between normal and rare events, and means that a value of $\underline{a} = -2.41$ must be regarded as arising from random causes. If more results were available the question could be fully solved, but Udovenko and Pasovskaya do not give these very necessary results and the question remains open. If it is accepted nevertheless that the method includes a systematic error and the equation rewritten in the form $X = 2.34 + 0.973y$, then the experimental results can be corrected slightly, as the figures adduced in the last column of Table 5 show.

TABLE 5

Results for the conductometric titration of KCl with sodium picrate

No.	KCl taken, in mg x_i	KCl found, in mg y_i	$\frac{y_i}{x_i} = Z_i$	$(Z_i - \bar{Z}) \cdot 10^5$	$(Z_i - \bar{Z})^2 \, 10^{10}$	X in mg
1	56.20	56.00	0.9964	-586	343396	56.82
2	80.30	79.30	0.9876	-1466	2149156	79.48
3	105.50	105.59	1.0010	-126	15876	105.1
4	120.58	122.23	1.0140	1174	1378276	121.2
5	150.72	152.53	1.0123	1004	1008016	150.6
Total	513.3	515.65	5.0113		$4,895 \cdot 10^{-4}$	
Mean			1.00226			

$$s^2 = 1.22 \cdot 10^{-4}$$

Of special interest in this example is a comparison of the tabular $s^2 = 1.22 \cdot 10^{-4}$ and the estimate of variance calculated for the values of $\underline{y} - \underline{Y}$ by formula (26) $s_y^2 = 0.606$. The ratio of these estimates of variance $T_H = 4970$, while for $k_1 = 3$ and $k_2 = 4$, the probability of $\underline{T}$ being greater or equal to 16.69 as a consequence of only random causes, is equal to 0.01. This means that $T_H = 4970$ cannot be explained by any random causes; here apparently the variance depends on the amount or concentration of the ion determined. Only the first steps have been made in investigating such systems.

D. The Evaluation of Micro Amounts on a Background of other Factors is Closely Related to the Examples Considered.

Problems of this type are of immense importance in the national economy, and the methods used and the results obtained should therefore be particularly carefully analyzed. As an example we shall consider results on the determination of CO in air by using the red oxide of mercury. This method essentially consists in measuring the loss in weight of a tube filled with HgO as a result of the reaction $HgO + CO \longrightarrow CO_2 + Hg$ at a temperature of 200°. The background in this case is determined by the partial dissociation of HgO at the temperature of the experiment and according to the authors' results [25] is characterized for pure air by the following series of results, calculated on CO: 2.6, 5.6, 5.6, 4.9, 5.0 μg (the values were calculated by us). It is pertinent to ask whether air contains CO when three replicates give results of 7.7, 8.3, and 6.8 μg/liter.

The solution of this question leads to an evaluation of the difference between two means by the formulas (22), (23), (24), and (25).

TABLE 6

Statistical treatment of the results for the determination of CO in air by a method based on the measurement of the loss in weight of a tube containing red HgO

No.	Control tests with pure air in μg CO/liter x_{1i}	$x_{1i} - \bar{x}_1$	$(x_{1i} - \bar{x}_1)^2$	No.	Results of the analysis of air in μg CO/liter x_{2j}	$x_{2j} - \bar{x}_2$	$(x_{2j} - \bar{x}_2)^2$
1	2.6	-2.2	4.84	1	7.7	0.1	0.01
2	5.6	0.8	0.64	2	8.3	0.7	0.49
3	5.6	0.8	0.64	3	6.8	-0.8	0.64
4	4.9	0.1	0.01				
5	5.0	0.2	0.04				
6	5.0	0.2	0.04				
Total	28.7		6.21		22.8		1.14
Mean	4.8				7.6		

$$s = \sqrt{\frac{6.21 + 1.14}{6 + 3 - 2}} = 1.02; \quad s_{\bar{x}} = 1.02\sqrt{\frac{6 + 3}{6 \cdot 3}} = 0.72;$$

$$t_1 = \frac{|4.8 - 7.6|}{0.72} = 3.87; \qquad k = 6 + 3 - 2 = 7;$$

$$p(|t| \geqslant 3.9) = 0.011$$

The calculations given in Table 6 give a value of $t_1 = 3.87$, the probability of the occurence of which as a result of random causes = 0.011. It is obvious that $t_1 = 3.87$ cannot be regarded as random and the difference between the means $\bar{x}_{1i}$ and $\bar{x}_{2j}$ is explained by the presence of CO in the air analyzed. The required value of the concentration of CO is determined with a reliability of 0.95 in the interval [5.7, 9.5 μg] since $t_{0.95} = 2.57$ for $k = 5$.

All determinations of trace elements and forensic analyses,etc., should be subjected to similar statistical treatment.

The examples given widen the scope of the questions touched upon in Gracheva's article [16] but far from exhaust all the cases of the application of statistical methods in chemical laboratories.

SUMMARY

1. The basic principles of the theory of errors, and mathematical statistics of direct importance for analytical chemistry,are set forth.

2. The fundamental formulas for the necessary calculations are adduced.

3. The characteristics which it is necessary to take into account when using mathematical statistics in analytical chemistry are noted.

4. Examples taken from periodical articles are treated in detail.

LITERATURE CITED

[1] S.N.Bernshtein, The Theory of Probability, State Chem. Press,Moscow-Leningrad 1946,p. 550.

[2] B.V.Gnedenko,A Course in the Theory of Probability, 373 (1950).

[3] V.I.Romanovsky, "Application of Mathematical Statistics in Experiment" State Tech. Press, Moscow-Leningrad,1947,p.228.

[4] A.M.Dlin,"Mathematical Statistics in Technics", "Soviet Science",Moscow, 1951,p. 268.

[5] Ya.N.Shpilrein, "Tables of Special Functions ,Moscow-Leningrad,1933, Part I p. 19.

[6] A.Worsing and J.Heffer "Methods of Treating Experimental Results",Moscow, 1949, p. 341.

[7] J.Scarborough "Numerical Methods of Mathematical Analysis",Moscow-Leningrad, 1934,p. 432.

[8] K.P.Yakovlev "Mathematical Treatment of the Results of Measurements",Moscow-Leningrad., 1950,p. 382.

[9] V.I.Roamnovsky, "Application of Mathematical Statistics in Experiment" State Tech. Press. Moscow-Leningrad, 1947 p. 236.

[10] V.I.Romanovsky, "Basic Problems of the Theory of Errors", State Tech. Press,Moscow-Leningrad,1947,p. 108.

[11] A.M.Dlin, "Mathematical Statistics in Technics", "Soviet Science" Moscow, 1951, p. 269.

[12] N.Arley and K.Bukh, "Introduction to the Theory of Probability and Mathematical Statistics", Moscow, 1951, p. 227, Table III. Here $\alpha = 1 - P$.

[13] V.I.Romanovsky, Application of mathematical statistics in experiment" State Tech. Press. Moscow-Leningrad, 1947, p. 240.

[14] A.M.Dlin, " Mathematical Statistics in Technics", "Soviet Science" Moscow, 1951, p. 270.

[15] A.V.Groshev and V.I.Ponosov, Factory Labs., 14, 669 (1948).

[16] E.G.Gracheva, J. Anal. Chem., 7, No. 1, 48 (1952).[1)]

[17] Barlow's Tables, Moscow, 1950.

[18] V.K.Zolotukhin, J. Anal. Chem. 6, No. 4, 249, (1951).

[19] A.I.Naumov, J. Anal. Chem. 6, No. 6, 353 (1951).

[20] R.B.Golubtsova, J. Anal. Chem. 6, No. 6, 357, (1951).

[21] W.J.Youden, Anal. Chem., 19, No. 12, 946, (1947).

[22] V.V.Udovenko and G.B.Pasovskaya, J. Anal. Chem. 7, No. 3, 159, (1952).[2)]

[23] V.V.Udovenko and G.B.Pasovskaya, J. Anal. Chem. 7, No. 3, 161, (1952).[3)]

[24] J.Mandel, Anal. Chem., 19, No. 12, 959 (1947).

[25] J.D.McCullough, R.A.Crane, A.O.Beckman, Anal. Chem., 19, No. 12, 999 (1947).

Received October 13, 1952

---

1) See Consultants Bureau translation, p. 51

2) See Consultants Bureau translation, p. 177

3) See Consultants Bureau translation, p. 181

THE ULTRAMICRO METHOD OF CHEMICAL ANALYSIS

PART I

I.P.Alimarin and M.N.Petrikova

(V.I.Vernadsky Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR, Moscow)

GENERAL OBSERVATIONS

The development of analytical chemistry during the last ten years has been characterized by the introduction into chemical practice of a new technique which has opened up possibilities of working with small amounts of material.

The ultramicro method of chemical analysis has attained very important scientific and practical significance recently. By means of this method it is possible to work with small volumes, as a result of which very small amounts of material can be studied while still maintaining the usual concentrations of solutions.

In the contemporary state of the development of science and experimental technique ultramicro chemical analysis is a natural continuation of the work of Russian scientists in the field of microchemistry. M.V.Lomonosov [1] was the first to use the microscope for chemical research in 1744. Somewhat later in 1798 the Russian chemist and crystallographer T.E.Lovits [2,3] developed this method of analysis and showed that a drop of solution is sufficeint for the determination of its qualitative composition by the method of microcrystalloscopy. In 1873 N.N.Akhmatov published his paper on "The application of the microscope to chemical research", in which he set forth a microchemical technique for the determination of cations. In 1868 K.A.Timiryazev [4] first introduced into practice gas micro- and ultramicro analysis. In 1929 B.Ormont [5] developed a method for the volumetric ultramicro titration of alkalis and acids. Ultramicro chemical analysis is being developed further in the Soviet Union at present. In particular the work of I.M.Korenman [6,7,8] may be mentioned. The work of the foreign scientists A.Benedetti-Pichler [9] and P.Kirk [10] are also worthy of note.

The great interest focussed recently on ultramicro chemical analysis may be explained by the new possibilities which this method opens up, by means of which very small quantities can be handled. Numerous examples can be quoted in various branches of science where the quantity of test material is so small that it can only be investigated by means of an ultramicro method. By applying this technique it is possible to determine the components of the products of synthesis of minerals at high pressures, which is a very important and interesting problem in experimental geochemistry and mineralogy. The ultramicro method can find a wide application in mineralogy and metallurgy in the analysis of inclusions. The composition of corrosion products can also be studied by means of the ultramicro method. The use of this technique has essential advantages in carrying out biological and clinical investigations. The study of the chemistry of isotopes is a field for the application of this method.

Although based on the same principles as those of the analysis of normal amounts of material the ultramicro method differs essentially in technique and scale. The relative scales of macro, micro, and ultramicro methods are compared in Table 1.

The technique for carrying out chemical operations is different for the ultramicro and macro scales, and even the ultramicro technique itself varies according to the volume containing the test material available. Chemical operations with volumes up to 0.001 ml are carried out with the naked eye or through a magnifying

TABLE 1

Method	Minimum volume of test solution		Minimum weight of element found as a precipitate		Minimum weight of sample for analysis	
	ml	λ	g	μg	g	μg
Macro method	1	1000	10^{-5}	10	10^{-1}	10^{5}
Micro method	10^{-2}	10	10^{-8}	10^{-2}	10^{-3}	10^{3}
Ultramicro method	10^{-6}	10^{-3}	10^{-9}	10^{-3}	10^{-6}	1

glass. Sometimes after carrying out some particular operation the reaction products are observed under the microscope. When the volumes are of the order of 10^{-3} to 10^{-6} ml all the basic operations are carried out on the object stage of the microscope. The tubes used are special forms of micro tubes (Fig.1) with a diameter of 0.5-1.0 mm made from capillaries. Liquids are transferred by means of micro pipets-capillaries with a drawn out end of diameter 0.01-0.02 mm (Fig. 1, 1). The pipet is provided with a piston set up (Fig. 2) for overcoming the surface tension which becomes quite appreciable when working with liquids in capillaries. The high rate of evaporation from small volumes necessitates working in a humid atmosphere which is attained by using a special box (Fig. 3). For the reliable manipulation of the volumes of solution or precipitate which are used in ultramicro chemistry, not only optical apparatus is used (microscope), which gives the impression of working at the scale of normal methods, but also mechanical aids which enable small amounts of material to be manipulated carefully under the microscope. These mechanical aids by means of which the necessary handling operations can be carried out are the movable object stage of the microscope on the one hand and a macromanipulator [9,11] on the other. The microscope and manipulator are both fixed to one plate. The humidity box with the glass micro tubes (Fig.4] are placed on the object stage of the microscope and the necessary instruments clamped in the manipulators. By means of an apparatus set up in this way (Fig. 5) ultramicro chemical determinations can be carried out.

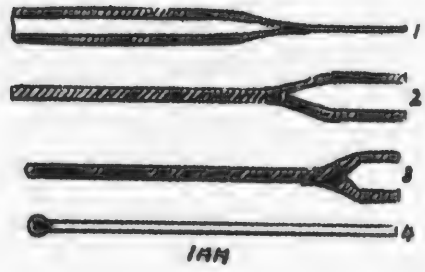


Fig. 1.Apparatus for ultramicro analysis:1 - micropipet; 2 - reaction tubes; 3 - capillary cone; 4 - measuring capillary.

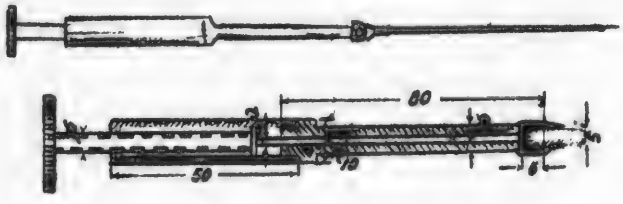


Fig. 2.Piston construction:A - general view (with a micropipet); B - longitudinal section.

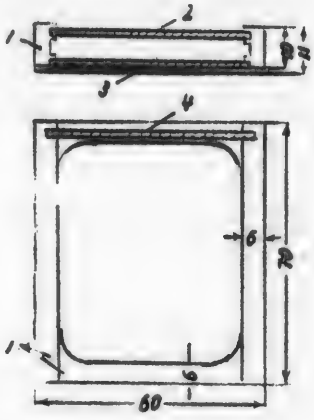


Fig. 3.Box (front view and view from above:1 - brass frame; 2, 3, 4 - glass cover, bottom and side.

Characteristics of the Ultramicro Chemical Method of Analysis

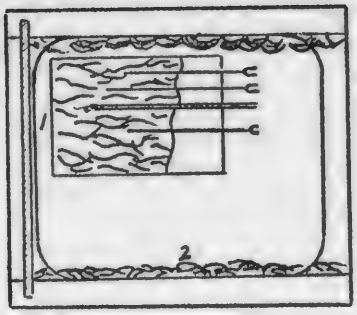


Fig. 4 Humidity Box with micro tube (view from above): 1 - glass plate with tubes; 2 - damp cotton wool.

The ultramicro method is the application of a technique of chemical experimentation which is specific and characteristic to the solution of analytical problems. By means of this technique the problems of the analysis of very small amounts of material can be solved easily and reliably.

Chemical reactions in which only a small number of molecules participates do not differ in any way from reactions in which large amounts of material are involved, as long as the number of reacting molecules ensures statistically the establishment of a chemical equilibrium. From this it follows that the concentration of reagents in the normal methods must be maintained; this is achieved by decreasing the volume when investigating small amounts of material.

Using the law of errors which is determined by statistical conditions and assuming that for a qualitative determination, an error of 10% is acceptable and for a quantitative determination an error of 0.1%, the limiting amount of material which is necessary for carrying out a chemical reaction can be calculated as follows;

$$100\frac{\sqrt{n}}{n} = \text{error in percent} \qquad (1)$$

where n is the number of reacting molecules. For a qualitative determination, assuming an average molecular weight of 60, we get;

$$10^{4}\frac{1}{n} = 10^{2}, \text{ from which } n = 100 \text{ molecules i.e.} \frac{60 \cdot 100}{6 \cdot 10^{23}} = 10^{-20} \text{g}$$

For a quantitative determination, assuming the same average molecular weight, we get.

$$10^{4}\frac{1}{n} = 10^{-2}, \text{ from which } n = 10^{6} \text{ molecules, i.e.,}$$

$$\frac{60 \cdot 10^{6}}{6 \cdot 10^{23}} = 10^{-16} \text{ g}$$

With amounts of material in excess of this limit any chemical operation can be carried out; whether this limit is exceeded or otherwise in principle depends on the level of development of experimental technique, and methods of observation. Thus, physico-chemical methods of registering reaction products enables the amount of material needed to be reduced by a much greater amount than visual methods (this applies primarily to volumetric and colorimetric determinations). The introduction of the electron microscope into practice opens up greater possibilities than hitherto of approaching the analysis of the limiting amount of material necessary for ensuring the establishment of chemical equilibrium.

One of the main conditions for carrying out these chemical determinations is the maintenance of the normal concentration of reactants by decreasing the weight and volume respectively. This leads to an increase (as compared with the macro methods) of the relative surface of the solution and the reaction tube, i.e., to

an increase in the surface of unit volume so that the surface decreases to a lesser degree than the volume. Table 2 illustrates this point by actual examples.

TABLE 2

Method	Diameter of tube, cm	Height of tube, cm	Surface of tube, cm^2	Vol. of solution, cm^3	Surface of unit volume, $S_{rel.}$	$\frac{S_{rel.\ ultra}}{S_{rel.\ macro}}$
Macro method	4.0	4.0	62.5	50.0	1.25	>20
Ultramicro method	0.2	0.2	0.16	0.006	26.6	

Since a relatively large surface of contact is established with the tube walls, the dissolved substance is adsorbed on them an also reacts with the material of the wall to a considerably greater extent than in the macro method. As a result, on the one hand there is a loss of part of the test material, and on the other it becomes contaminated. The loss as a result of adsorption on the glass attains very large values for a number of elements in alkaline media. It must also be borne in mind that in practice when using ultramicro techniques it is necessary to concentrate small amounts of material which originally are dispersed in large volumes, in order that one can handle them with the respective technique. In such cases the final solutions which are obtained usually require a preliminary purification from appreciable amounts of other or interfering compounds. These compounds, although at first present only in insignificant amounts - they originate either from the walls of the tube or from the reagents - become concentrated on evaporation. E.g., on evaporating 25 ml of a dilute nitric acid to $5 \cdot 10^{-3}$ - 10^{-2} ml considerable amounts of salts of iron (although the acid was preliminarily distilled), sodium and calcium were obtained as well as a large precipitate of silicic acid (Fig. 6).[1] It is understandable that under these conditions the purity of the original reagents and the stability of the material of the walls of the tube to the effect of the reagents employed acquire a special significance.

The increase in the relative surface which occurs in ultramicro methods in a number of cases affects the velocity of crystallization from solution and the crystal form.

On switching over to the ultramicro scale the free surface of the liquid increases relatively because of the large curvature of the meniscus in the capillaries. As a result the evaporation velocities of solutions which is directly proportional to the free surface of the liquid here attains a considerable value. The evaporation velocity at atmospheric pressure is expressed approximately by the formula

$$v = KS(P - p), \qquad (2)$$

where S - is the free surface of the liquid; P - the pressure of the saturated vapors at a given temperature; p - the pressure of the vapors above the liquid and K - a constant. According to the kinetic theory the change in vapor pressure ΔP with the curvature of the liquid surface is expressed by the equation:

$$\frac{\Delta P}{P} = \frac{2\sigma M}{rdRT}, \qquad (3)$$

where σ - is the surface tension; d - the density of the liquid; r - the radius of curvature; M - the molecular weight; R - the universal constant; and T - the absolute temperature. It is evident that liquids which wet the capillary, as a result of the large curvature of the concave surface, have a considerably lower vapor pressure in the capillary than in wide tubes. Nevertheless evaporation is incomparably quicker, since the free surface of the liquids increases relatively, to a considerably greater extent than the vapor pressure decreases. E.g., the free surface of a liquid contained in a capillary of diameter 0.6 mm amounts to about 0.6 mm^2 and not 0.3 mm^2 as for a flat surface of the same diameter, while the

1) See plate, p. 431.

vapor tension above the meniscus with the corresponding curvature is lowered 5%. In addition the solution in a capillary is under considerably better conditions for heat transfer.

In order to decrease the evaporation velocity from capillaries when using an ultramicro method the work is carried out in a humid atmosphere. Aqueous solutions of salts which have a lower vapor tension than water evaporate under similar conditions somewhat slower than water, but not to such an extent that it excludes the necessity of working in a humid atmosphere. The volume of saturated salt solutions contained in capillaries increases rapidly when working in a humid atmosphere as a result of an evening out of the vapor pressure in the system vapor above pure water (humid atmosphere) – vapor above the saturated solution in the capillary. The hygroscopicity of the dissolved salt is also of significance. Saturated solutions of salts should not therefore be handled in a humid atmosphere. The figures given in Table 3 confirm what has just been said.

TABLE 3

Substance	Diameter of capillary in mm	Volume of solution in mm^3	% Change in volume in min. to total volume	
			Ordinary Atmosphere	Humid Atmosphere
Water	0.12	0.02	−1.0	−0.1
1 M Potassium nitrate	0.12	0.02	−0.4	−0.06
Saturated calcium chloride solution	0.12	0.02	+0.02	+0.6

Organic liquids which have to be used for the preparation of solutions, or for extractions, evaporate particularly rapidly as a result of their low heat of vaporization or their high vapor pressure. Such compounds as ether and chloroform, which have particularly high vapor pressures, are ejected from thin capillaries with one end sealed by the action of their own vapors forming a rapidly evaporating drop at the open end of the capillary. The evaporation of organic liquids can be cut down by working in an atmosphere of the vapor of the respective liquid.

The increase in the surface of a liquid relative to its volume has its own consequences, in addition to an increase in adsorption of the substance from solution by the walls of the tube and of an increase in evaporation rate, the surface tension also increases and attains a considerable value when working with capillaries. This fact is of major importance in developing the experimental technique of ultramicro methods. On one hand the position is complicated by the necessity of overcoming surface tension in transferring liquid from capillary to capillary, while on the other hand this fact excludes the possibility of loss of solution by spilling; and also, as a result of the stable (within the limits of evaporation velocity) position of the meniscus, it enables the amount of solution to be measured accurately. The cleanliness of the surface of the liquid plays an important part in working with capillaries. The presence of surface active agents in the solution increases the wettability of the glass surface by the solution and leads to experimental errors. Solutions of salts have a higher surface tension than water, the surface tension increasing approximately in proportion to the number of equivalents of dissolved salt. This increase in surface tension explains the creeping of salts (e.g., NH_4Cl), which is a serious handicap when working with capillaries. The creeping of precipitates along the glass also interferes with work (e.g., the precipitate of nickel dimethylglyoxime). As a result of the increase in surface tension the evolution of gas from solutions contained in capillaries occurs in a totally different way from that in macro methods; a bubble of gas which has been formed often does not reach the surface of the liquid but remains where it has been

formed and with time assumes greater proportions and finally divides the solution into two isolated parts. The horizontal position of the capillaries help the surface tension to give rise to this state of affairs. Heating the liquid to boiling, which is characterized by the appearance of bubbles of vapor under the liquid level, followed by subsequent evolution, is excluded in ultramicro methods in contrast to macro methods, since together with intensive vapor formation, the surface tension decreases with increasing temperature, with the overall result that the liquid is expelled from the capillary particularly easily.

All the same the ultramicroscopic methods still have great advantages. By enabling small amounts of material to be determined, the method, at the same time, in a number of cases gives an increased sensitivity as compared with the macro methods. This can be illustrated by considering the detection of an element in the form of one of its compounds.

The sensitivity of a reaction is characterized by two mutually related quantities; the limit of identification and the minimum concentration. The limit of identification is the smallest amount of a substance which can still be detected by a given reagent under the definite experimental conditions used for examining the reaction products. The minimum concentration shows at what dilution of the test solution a reaction still gives positive results under certain experimental conditions. It is expressed by the ratio of unit weight of material detected in solution to the weight or volume of solvent. Knowing the volume in which the reaction has been carried out, it is possible to calculate the minimum concentration from the limit of identification and vice versa by the relations:

$$C_{min.} = 1 : \frac{V}{m}, \quad m = C_{min.} \cdot V, \qquad (4)$$

where $\underline{m}$ is the limit of identification in g; $\underline{V}$ is the volume of solution in ml; $C_{min.}$ - the minimum concentration.

By varying the experimental conditions it is possible to increase the sensitivity of a given determination.

The intensity of the color of a solution depends on the presence of a corresponding amount of a colored substance in the path of the rays of light. The nature of a colored substance is characterized by the value of its extinction coefficient. The sensitivity of a color reaction indicates the least amount of a colored substance located in the path of the light necessary to give an observable color to the solution. If it is assumed that the Lambert-Beer laws $E = KCl$ still holds at very low concentrations of substance, then one can talk of a minimum concentration for a definite reaction only for a layer of a given thickness, so that the concept of "minimum concentration" acquires a definite meaning. For a given colored substance (K = constant) and defined conditions of observation, the product $Cl = E$ is a constant, from which it follows that the value of the minimum concentration is determined by the nature of the colored substance and the selected length of the path of light; it does not depend on any other parameter, not even on the cross section of the column of liquid through which the light passes. The sensitivity of a reaction is determined by the limit of identification as well as by the minimum concentration

$$m = C_{min.} \cdot V, \qquad (4)$$

But $V = \underline{l} \cdot S$ where $\underline{l}$ is the selected thickness of the layer of solution (the length of the path of light); $\underline{S}$ - the cross section of a column of solution from which $\underline{m} = C_{min.} \cdot \underline{l} \cdot S$, i.e., the limit of identification is proportional to the cross section of the solution.

For the observation of color in the ultramicroscopic method coloriscopic capillaries are used in which the thickness of the layer of the colored solution

is commensurable with that in a macro method, but the section is considerably smaller so that the limit of identification can be essentially increased. The section of a column of the solution in the ultramicro method is usually 10^4 times smaller than in a macro method. The same ratio therefore holds for the limits of identification in the two respective methods. The minimum concentration which is independent of the cross-section of the solution for commensurable thicknesses, being related to unit length, is equal for both the macro and ultramicro methods. Nevertheless if columns of solution of different cross-sections are used for observation the Lambert-Beer law is not followed, as a result of some physiological peculiarities of the eye; thus if two columns of different cross-sections but containing colored solutions of the same concentration are examined under similar conditions, it appears that the one with the larger cross-section is colored more intensely than the other. It is possible therefore for a color which is unobservable in a column of lesser cross-section to be observed by the eye in a column with a greater cross-section.

This is particularly marked in ultramicroscopic determinations and is bound up with the use of capillaries the diameters of which may differ among themselves by 2, 3, 4 or more times.

Such are the general features, principal characteristics , drawbacks, and merits of the ultramicroscopic chemical method of analysis, which is opening up new possibilities for chemists to investigate the composition of substances.

LITERATURE CITED

[1] S.Sobol, "The History of the Microscope and Microscopic Research in Russia in the 18th Century," Acad. Sci. USSR, 1949.

[2] G.Lemlein, E.Tsekhnovitser " A Contribution to the History of the Origin of Microchemical Analysis, Archives of history and technics, Series 1, No. 4, Acad. Sci. USSR (1934).

[3] A.Batalin, "From the History of Microchemical Analysis in Russia" Journal of Chemistry, 4, 5, 308 (1939).

[4] K.Timiryazev, "Collected Works" Vol. 1, 374 (1937) Vol.2, 409 (1937).

[5] B.Ormont, J. Russ. Phys. Chem. Soc., 355, (1929).

[6] I.Korenman, "Quantitative Microchemical Analysis", State Chem. Press, 1949.

[7] I.Korenman, "Symposium on Quantitative Ultramicroanalysis", Gorky, 1949.

[8] I.Korenman, E.Gronsberg, "Proc. Commission on Anal. Chem.", 3/6/, 150 (1951).

[9] A.Bendetti-Pikhler, "Technique of Inorganic Microanalysis, I.L. 1951.

[10] P.Kirk, "Quantitative Ultramicroanalysis ", 1952.

[11] P.Fonbryun, "Methods of Micromanipulation", 1951.

Received September 9, 1952

SPECTROPHOTOMETRY IN CHEMICAL ANALYSIS

S.I.Sinyakova and N.P.Ivanov

V.I.Vernadsky Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR, Moscow.

Spectrophotometry has found a very wide application in chemical research including the solution of a number of analytical problems. By means of spectrophotometry the structure of a number of organic and inorganic compounds has been studied, and a number of analytical methods for both organic and inorganic compounds developed. Nevertheless, until recently the development of the spectrophotometric method of analysis has been hindered by the absence of the requisite apparatus. With the appearance of the Russian spectrophotometer, the SF, wide possibilities have been opened up for chemists of using this apparatus in the various branches of chemistry: for the study of the composition of complex compounds, organic compounds, and for the analysis of various substances, mainly in the presence of several components. By means of a spectrophotometer it is possible in a number of cases, to establish in addition the quantitative relationships of different valency states of the same element in solution. E.g., it is possible to determine the amounts of vanadium (V) and vanadium (IV), present in solution also containing chromium (III) and chromium (IV), etc..

Spectrophotometry widens the field of application of organic reagents in the analysis of inorganic compounds, since it enables several colored compounds to be determined in one solution.

The advantages of the spectrophotometric method of analysis as compared to other photometric methods are the possibilities of analyzing multicomponent systems. In addition, the sensitivity of the determination is increased, since the measurement is carried out at wave lengths which correspond to maximum absorption. The accuracy of the determination also increases, particularly when the apparatus is fitted for photoelectric registration. The SF is of this type.

Even greater possibilities are opened up for analytical chemists if absorption spectra in the ultraviolet and infra red are used, because thereby colorless compounds can be determined. The SF enables work to be carried out in the ultraviolet region by using a hydrogen lamp as the light source. In the ultraviolet region as many as 4 components can be determined quantitatively when present together.

In the present article the authors do not intend to give a complete picture of the spectrophotometric work; their idea is to show by means of a number of examples the various problems solved by means of spectophotometry and also to demonstrate its advantages by actual experimental data.

Qualitative and Quantitative Methods of Analysis by Means of Absorption Spectra

Qualitative analysis by means of absorption spectra is based on a comparison of the spectrum of an unknown solution with the absorption spectra of a solution containing known components.

It is evident that in order to carry out qualitative analysis it is necessary to have a collection of absorption curves for the group of substances being analyzed which have been either obtained experimentally in the laboratory or from literature sources. In general for the qualitative analysis of solutions of inorganic compounds

for which no preliminary results are available, turning to the absorption spectra is hardly reasonable because of the considerable dependence of these on a multitude of factors.

Quantitative methods of spectrophotometric analysis are based on the Lambert-Beer absorption law. A detailed exposition of this law is given in a number of textbooks [1, 2, 3, 4, 5].

The Beer law is only applicable for cases where the absorption coefficient is independent of concentration. However, such an independence of the absorption coefficient and consequently of the absorption spectra is only obtained for small concentration changes. The range of concentrations within which a solution obeys the Beer law is determined experimentally in each individual case.

Deviations from the Beer law can arise from a number of causes: the dissociation of colored complexes in dilute solution [6]; the change of state of intermolecular dissociation for changes in the pH [7]; displacement of the absorption maximum with concentration changes, and in some cases as a result of the formation of new complexes [2].

The determination of the concentration of one-component systems is carried out on the basis of the Lambert-Beer law, from which it follows that $c = D/K$, where K is the extinction coefficient determined by measuring the optical density of a solution with a given concentration. In practice it is more usual to use a graphic relation between extinction coefficient and concentration. The most simple method is the method of additions, which is applied to the analysis of solutions for which there are existing guiding results on the concentration. In this case a known amount of the component being determined is added to the solution with unknown concentration c_x. The concentration required is then determined by the formula

$$c_x = c_a \frac{D_x}{D_{x+a} - D_x} = c_a \frac{\log T_x}{\log \frac{T_{x+a}}{T_x}},$$

where D_x and T_x are the optical density and the transmission of the solution with a known concentration, and D_{x+a} and T_{x+a} the optical density and transmission for the same solution after the addition of a known weight of the test material.

In recent years the differential method has found application. This method consists in measuring the extinction of the test solution with respect to a standard solution of the same compound but of know concentration [8].

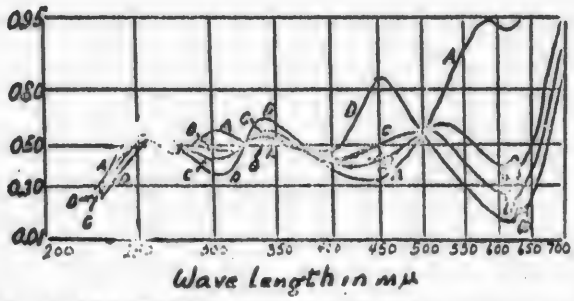


Fig. 1. Absorption curves for bromothymol blue at various pH's Solvent, water. A - pH 5.45; B - pH 6.95; C - pH 7.50; D - pH 11.60

In carrying out an analysis the choice of wave length to be used is very important. In general, measurements are made at those wave lengths which correspond to maximum absorption. Where the spectra consists of several maxima, the widest of the maxima should be chosen, because both the change in slit width of the spectrophotometer and the set up used for adjusting the wave lengths used will have the least effect. For solutions the absorption spectra of which are strongly dependent on the acid-

ity, it is convenient to use the point of intersection of the absorption curves for different pH's, e.g., the wave length of 501 mμ on Fig. 1 [9].

Determinations of the concentrations of a two-component solution are carried out at 2 wave lengths; in the case where they do not affect one another the following equations can be used

$$D_{\lambda_1} = K_{a\lambda_1} c_a + K_{b\lambda_1} c_b \ , \qquad (1)$$
$$D_{\lambda_2} = K_{a\lambda_2} c_a + K_{b\lambda_2} c_b \ .$$

The coefficients $K_{a\lambda 1,2}$ and $K_{b\lambda 1,2}$ are determined by measuring the optical densities $D_{\lambda 1}$ and $D_{\lambda 2}$ of solutions of known concentrations.

The criteria for the selection of the wave lengths λ_1 and λ_2 are the two conditions:

1) The values D_{λ_1} and D_{λ_2} should lie within the range 0.3 to 1 (the transmissions respectively in the range 10 - 50%) [2].

2) The ratios $K_{a\lambda_1}/K_{b\lambda_1}$ and $K_{b\lambda_2}/K_{a\lambda_2}$, i.e., the ratios of the absorption coefficients of the two components should be a maximum [9].

When measurements are made at wave lengths satisfying the given conditions the relative error $\Delta c/c$ will be a minimum.

In special cases the analysis can be simplified considerably.

Thus, if there is a part of the absorption spectra where only one of the components is absorbed, then the concentration can be determined by the relations

$$c_a = \frac{D_{\lambda_2}}{K_{a\lambda_2}} \qquad c_b = \frac{K_{a\lambda_1} D_{\lambda_2} - K_{a\lambda_2} D_{\lambda_1}}{K_{a\lambda_2} K_{b\lambda_1}}$$

If there is such a part for each component, then the analysis can be carried out independently by the equations:

$$D_{\lambda_1} = K_{a\lambda_1} c_a \ , \quad D_{\lambda_2} = K_{b\lambda_2} c_b \ .$$

The quantitative analysis of solutions containing components which mutually affect each other is carried out by means of an empirical graph which expresses the relation between the optical density and the various concentrations of the two components, or by removing the influence of one of these components by changing the pH or the valency, and also by binding it as a complex.

A Description of the SF-11 Spectrophotometer

The non-registering photoelectric quartz spectrophotometer SF-11 is designed for the determination of optical densities in the wave length range from 2,200-11,000 A.

The optical set up of the spectrophotometer is shown schematically in Fig. 2.

Light from a source 1 [incandescent lamp (glower) for visible light and a hydrogen lamp for the ultraviolet] is focussed by a condensing mirror 2 on to the entrance slit 4.

The divergent light beam which passes throught the slit is converted by the concave mirror 5 into a parallel beam and reflected on to prism 6, one surface of which is coated with aluminum. The divergent light reflected by the prism is focussed by mirror 5 on to the slit 4 which is the exit slit of the monochromator. After passing throught the cell 7 containing the test solution, the part of the spectra chopped off by the slit 4 falls on the photoelement 8.

The linear dispersion of the spectrophotometer in the region 8000 - 4000 A increases from 65 to 10 mμ/mm. Thus the chopped off part of the continuous spectra for a slit width less than 0.1 mm does not exceed 6.5 mμ/mm.

Since the half width of the absorption band for solutions of inorganic compounds in the majority of cases amounts to 100 - 150 mμ, the light flow passing through the solution can be regarded as monochromatic.

The external appearance of the SF-11 is shown in Fig. 3.[1)]

The operating procedure for the SF-11 is very simple. Measurement of the whole absorption spectra in the 400 - 1000 mμ range at intervals of 20 - 25 mμ only takes 10 - 15 minutes, while three measurements of the optical density at the selected wave length takes 2 - 3 minutes.

The apparatus gives completely satisfactory reproducibility-deviations in repeated measurements do not exceed 0.8 - 1% - while the mean deviation only amounts to 0.4 - 0.5%. For errors obtained with different spectrophotometers see [10].

Apart from spectrophotometers other apparatus [83, 84, 85] are used for the analysis of two and three components by means of their absorption spectra.

The Use of Spectrophotometry in Chemistry

Spectrophotometric methods are widely used in all branches of chemistry. A large amount of work on the structure of organic compounds has been published by Soviet scientists. Thus the absorption spectra of several intermediate products and azo-dyes of the naphthalene series [11] and a number of derivatives of di- and tri-phenylmethane have been studied, whereby a number of important conclusions could be made as to their structure [12]. The absorption spectra of benzene derivatives [13, 14], heterocyclic compounds of rhodamine and N-phenylrhodamine [15], and of phenylhydrazine derivatives have been studied.

A number of papers by Soviet scientists has been devoted to the spectrophotometric investigation of biuret complexes, enabling an approach to be made to protein structure [17, 18, 19, 20]. Several research workers have used the spectrophotometer for the determination of the pH of solutions [21, 22] by means of calibration curves $D = f(pH)$.

The spectrophotometric method in the red part of the spectrum has also been used for selecting the ratios of standard solutions of cobalt chloride and ferric chloride in order to imitate the color of Bogen's indicator [23]. A lot of work has been devoted to the study of the composition of complex compounds by means of the spectrophotometer, e.g., the absorption spectra of cobalto-(II)-halide complexes in various organic solvents: in ethyl, butyl, and propyl alcohol and in acetone have been studied. It was shown that the complexes $CoCl_4^{2-}$ and $CoBr_4^{2-}$ [24] exist in acetone. Complexes of copper (II) with sulfosalicylic acid have also been examined with the spectrophotometer. It was shown that pH affects the absorption spectra of similar complexes [25]. It was established that complexes CuR or CuR_2^{2-} could exist either independently or together in solution according to the pH. [26].

The interaction of halogens dissolved in carbon tetrachloride [27] has been examined, and a number of other investigations carried out.

A Short Review of Spectrophotometric Methods of Analysis

For analytical chemists it is the application of the spectrophotometric method to the analysis of organic and inorganic compounds which is of the greatest interest. There are hundreds of papers on this topic. In this short review therefore we shall confine ourselves to the most typical examples of the application of this method, analysis of organic compounds being only touched on very briefly.

1) See plate p. 431.

Analysis of Organic Compounds

A spectrophotometric method has been developed for the determination of m-nitrobenzene and trinitrotoluene by treating them with alkali in acetone solution [28]. A quantitative method has also been proposed for the determination of azotols and aromatic diazo compounds. The absorption spectra of these compounds have been studied with the help of a photoelectric-spectrophotometer in the wave length range 220-1000 mμ in the near ultraviolet [29]. Spectrophotometric methods have been proposed for the determination of acetaldehyde in blood [30], for the determination of formaldehyde and furfurol when present together (by the absorption of a colored compound with Schiff's compound)[31], for diacetyl (by the absorption of a colored compound obtained by interaction with chromotropic acid in sulfuric acid at 570 mμ) [32], for phthalic acid (by measuring absorption in the ultraviolet region at 276 mμ) [33], for 8-hydroxyquinoline and its products (by absorption of their complexes with Fe^{3+} at 650 mμ [34], for anthracene [35], typtophane [36], nicotine (by absorption in the ultraviolet region at 260 mμ [37],and for a number of other compounds.

Analysis of Inorganic Compounds

Spectrophotometric methods have been worked out for the determination of a number of elements and inorganic compounds. In this review it is impossible to include even a significant amount of the work which has been devoted to this question in recent years. We shall therefore confine ourselves to a few typical examples of the determination of one, two and three components in solution.

The Determination of One Component

Copper. Copper has been determined spectrophotometrically by measuring the absorption of the complex formed between Cu (II) and rubeanic acid [38] or the absorption of thecomplex formed between Cu (II) and benzoinoxime at 440 mμ after extraction with chloroform. Copper has been determined by the latter method in iron alloys with a mean error of 0.005%. Ni and Co interfere [39].

Iron. Iron has been determined in iron ores containing up to 58% Fe by measuring the absorption of the complex formed between Fe^{3+} and 5-hydroxy-3-(hydroxymethyl)-1,4-pyrone from solutions with pH 6.3 - 6.5 at 440 mμ.

The optimum concentration is 0.0001 - 0.0005 mg Fe/ml. The accuracy of the method is 0.05%, despite the high dilution of the test solution [40]

Iron has also been determined in high melting alloys by measuring the maximum absorption of the complex between Fe^{2+} and 1-10 phenanthroline at 490 mμ [41].

Aluminum. For the spectrophotometric determination of aluminum in steels the complex of aluminum with hydroxyquinoline extracted in chloroform has been used. A colorimetric variation of the method was proposed by Mervel [43] and worked out by Kuskova for the determination of aluminum in steels [44]. The absorption of the chloroform solution of the complex was measured at 390 mμ. The accuracy of the method is ca. 5% for an Al content of 0.005 - 0.1% [45].

Beryllium. A spectrophotometric method has been proposed for the determination of small amounts of beryllium (0.0015 - 0.23%) in aluminum, based on the measurement of the absorption of the complex formed between beryllium and sulfosalicylic acid $[Be(C_6H_3SO_3OCO_2)_2]^{4-}$ at 317 mμ. Interference from Al is removed by combining the Al with ethylenediaminetetracetic acid or its salts. Fe and Cu interfere [42].

Lead. Lead has been determined in copper by means of the absorption of its complex with dithizone [46]. Dithizone has also been used for the spectrophotometric determination of other metals [47].

Nickel. For the determination of Ni the absorption of its complex with 1,2-cycloheptanedionedioxime (heptoxime) has been used.

The absorption curve has 2 maxima, the position of which depend on the pH of the solution and the time from the moment of inception of the reaction. This reagent has been shown to have no advantages over dimethylglyoxime [48]. A similar method has been proposed for the determination of Ni in which the absorption of the complex of Ni with nioxime (1,2-cyclohexanedionedioxime) was measured [49].

Cobalt. As an example of the spectrophotometric determination of cobalt, its determination in atmospheric dust by measurement of the absorption of its complex with nitroso-R-salt [50] may be quoted. This complex was suggested by Malyuga for the colorimetric determination of cobalt [51].

Vanadium. For the determination of vanadium in iron alloys the absorption of the phosphovanadotungstate complex first suggested by A.P.Vinogradov for the colorimetric determination of V [52] has been used. The maximum absorption of the complex is at 365 mμ; for analysis however it is more convenient to take measurements at 480 mμ [53].

It has been suggested that vanadium can be determined by measurement of the absorption of its complex salt with hydrogen peroxide in the ultraviolet at 290 mμ. For measurements in the ultraviolet the Beer law is obeyed for solutions with concentrations of from 0 to 0.125 mg/ml V. Ti and $Cr_2O_7^{2-}$ interfere to a lesser degree than when the measurements are made in the visible spectrum [54].

Molybdenum. Molybdenum in steel has been determined by the measurement of the absorption of the complex between molybdate and phenylhydrazine in acid solution at 505 mμ. 0.002-0.010 mg Mo can be determined with an accuracy of 2.9% relative units [55].

Chromium. For the micro determination of Cr in skin the absorption of the reaction product between chromate and diphenylcarbazone at ca. 530 mμ[1] has been measured [56].

Tellurium. Tellurium has been determined by measuring the absorption of the iodotellurate complex at 335 mμ, although this complex has an even greater maximum at 285 mμ. The Beer law however is only obeyed at 335 mμ, and then only within narrow concentration limits 0.2-2 μg Te/ml [57]

Rare Earth Metals. The possibility of spectrophotometric determination of the rare earth elements is of special interest because the methods of analysis for this group are very limited (usually X-ray spectrographic analysis is used). An investigation of the absorption spectra of solutions of chlorides, sulfates, nitrates, perchlorates and acetates of 11 rare earth elements in the wave length region 220 - 1000 mμ showed that the absorption spectra of the different salts of the same elements were almost identical. Some displacement of the spectra were observed for neodymium, samarium, europium, and gadolinium in solutions of their acetates. For analytical purposes it is more convenient to use the wave lengths adduced in Table 1 for each of the rare earth elements in the presence of other elements of this group since in this wave length interval Sc, Y, La, and Th do not absorb and the others do not interfere so much.

Mention may be made here of an indirect method for the determination of calcium in blood by measuring the excess Ce (IV) which has to be added to oxidize the oxalate combined with the calcium. The absorption of Ce (IV) was measured at 315 or 390 mμ. The mean error is ±2.2% [59].

TABLE 1

Element	λ in Å	Element	λ in Å
Pr	4445	Gd	2728
Nd	5218	Er	3792
Sm	4020	Tu	6825
Eu	3939	Yb	9750

1) Measurements were made on a Pulfrich photometer.

Elements of the Platinum Group

A number of spectrophotometric methods have been proposed for the quantitative determination of elements of ths platinum group.

It has been proposed that platinum can be determined by means of the absorption of the yellow color of the solution obtained by the interaction of $PtCl_4$ and $SnCl_2$. Aqueous solution were measured at 400 - 300 mμ. Solutions in amyl acetate have also been measured, but they are less stable. The differential method of measuring the absorption was used. The accuracy of the method is completely satisfactory [8]

A method has been proposed for the determination of ruthenium as potassium ruthenate in 2 M KOH solution [60]. The absorption spectra of potassium ruthenate has a maximum at 465 mμ. The Beer law is obeyed if the ruthenium content is within the limits $1 \cdot 10^{-4}$ - $4 \cdot 10^{-4}$ M. Pt, Ir, Pd and Rh do not interfere since they do not exhibit an appreciable absorption at 400 mμ. In addition they do not fuse easily with alkali (an operation necessary to get the ruthenium into solution).

For the spectrophotometric determination of osmium, measurements of the absorption of the rose-red colored complex of osmium (VIII) with thiourea in acid solution has been adopted [61]. The maximum absorption of this complex is at 480 mμ, nevertheless it is recommended that quantitative determinations of osmium should be carried out at 540 mμ, since palladium does not interfere at this wave length.

A spectrophotometric method has also been developed for the determination of rhodium (III) with sodium hypochlorite at a pH of 4.7-7.2 [62]. Maximum absorption occurs at 665 mμ; Pd, Pt, Au, Fe, Cr and Ni do not interfere even for considerable amounts of them, while Ru, Os, Ir, Co, Mn and Cu do not interfere if their contents are low compared to that of rhodium. Only iodides and iodates of the common anions interfere. It is best to determine rhodium in amounts of $5 \cdot 10^{-4}$ - $2 \cdot 10^{-3}$%. The experimental error is ~0.6% relative units.

Phosphorus. Phosphorus has been determined spectrophotometrically after formation of phosphomolybdic acid $H_3[P(Mo_3O_{10})_4]$ in sulfuric acid at a pH of ca. 1. The absorption of this acid is measured at 380, 400 and 420 mμ. Si and Fe interfere [63].

Silicon. For the determination of silicon in vanadium and uranium the absorption of the silicomolybdic complex is measured at 390 mμ after separation of metals with cupferron. The Beer law is obeyed for Si contents of 0.02 - 0.28 mg/100 ml. The reproducibility is ±0.004 mg Si [81].

Nitrates. Nitrates have been spectrophotometrically determined in galvanized silver baths for amounts of nitrate of 0 - 120 g/liter. The maximum absorption of KNO_3 was measured in the ultraviolet at 302.5 mμ. The maximum is displaced slightly with change in concentration of NO_3^-. The accuracy of the method is ±2% relative units [64].

Flurine. It has been proposed that fluorine in sea water be determined by measuring the absorption at 512 mμ of solutions containing the indicator zirconalizarin-sulfonate and adjusted to pH 4. The fluorine content is determined by the decrease in absorption of the indicator. Borates, Fe, PO_4^{2-} do not interfere. [65].

Iodine. Spectrophotometric determination of iodine in rocks, soils and other natural objects has been carried out by measurement of the absorption of the reaction products of iodine with starch at 575 mμ in sulfuric acid solution. The iodine is initially oxidized by $KMnO_4$ to IO_3^-, which then reacts in sulfuric acid solution with KI in the presence of starch to liberate iodine. The mean error is 0.9%, maximum error 2.5% [66].

Hydrogen Sulfide. As an example of the determination of a gas spectrophotometrically, we quote the method developed for H_2S which is based on the absorption of H_2S in a solution of zincate to form ZnS which is then reacted with an acid

solution of p-aminodimethylaniline with the addition of $FeCl_3$. The absorption of the methylene blue formed is measured at 670 or 750 mμ. The accuracy of the method is about ±3.0% for a H_2S content of 0.1 - 0.2 mg H_2S [67].

The Determination of Two Components

One of the first to use the spectrophotometer for the analysis of mixtures containing two colored components was Uspensky [68]. Babko and Korsun [87] have considered in detail the conditions for colorimetric determination in mixtures of two colored compounds. Komar [88] has proposed simple methods for calculating the equilibrium constant and the molecular absorption coefficients of most colored complex compounds used in spectrophotometric analysis, and also proposed methods for the spectrophotometric analysis of mixtures of compounds which do not obey Beer's law.

Below we have adduced a few examples of the spectrophotometric determination of two components in various industrial products.

Chromium and Manganese. Maltsev and Davydov [69] have worked out a spectrophotometric determination of chromium and manganese in steels and ferro-alloys based on the oxidation of Cr and Mn respectively to $K_2Cr_2O_7$ and $KMnO_4$. The maximum absorption of $K_2Cr_2O_7$ is located at 430 - 450 mμ while that of $KMnO_4$ is at 510 - 550 mμ. $KMnO_4$ can be determined directly at 530 mμ, since the absorption of $K_2Cr_2O_7$ at 530 mμ is negligible; but in the case of $K_2Cr_2O_7$, it is necessary to apply a correction to its absorption because at 450 mμ $KMnO_4$ exhibits some absorption. This method was subsequently used by other investigators [70, 71][1].

Bichromate and Chromate. A method has also been proposed for the spectrophotometric determination of $K_2Cr_2O_7$ in solutions saturated with respect to $K_2Cr_2O_7$ and K_2CrO_4. The absorption is measured at 425-500 mμ for which there is a difference in absorption for CrO_4^{2-} and $Cr_2O_7^{2-}$. A calibration curve is constructed at 528 mμ [72] for the absorption of mixtures of CrO_4^{2-} and $Cr_2O_7^{2-}$ for various ratios of these ions and at a constant chromium content.

Iron and Titanium. These two elements have been determined in cathodic nickel. Tyron (Na_2-1,2-dihydroxybenzene-3,5-bisulfonate) was the reagent used. The absorption of the iron complex was measured at 560 mμ and that of the titanium complex at 399 mμ after destruction of the iron complex by means of $Na_2S_2O_4$. The accuracy of the method is reasonably good. [73].

Titanium and Vanadium. Babko and Volkova have carried out a detailed investigation of the titanium and vanadium complexes of hydrogen peroxide with a Pulfrich photometer. They have proposed a photometric determination of these elements in their mixtures.

Iron and Aluminum. A spectrophotometric method has also been worked out for Fe and Al based on the measurement of the absorption of their complexes with ferron. The absorption of the iron complex was measured at 600 mμ while that of the aluminum complex was measured at 370 mμ [74].

Molybdenum and Niobium. Mo and Nb have also been determined spectrophotometrically when present together. Mo is colored with thiocyanate and Nb with H_2O_2. [75].

Determination of Three Components

There are a number of papers on the spectrophotometric determination of three component mixtures, but the accuracy hitherto obtained is not very high.

---

1) Babko and Korsun demonstrated the possibility of determining $K_2Cr_2O_7$ and $KMnO_4$ in their mixtures by means of a Dubosq colorimeter in conjunction with selected filters.

Titanium, Vanadium, and Molybdenum. For the determination of titanium, molybdenum and vanadium when present together the absorption of the complexes formed between these elements and H_2O_2 in perchloric at 410 mμ (Ti), 460 mμ (V) and 330 mμ (Mo) was determined. However as the author points out this method does not pretend to be a substitute for other methods of determining V and Mo [76].

Cobalt, Copper, and Iron. A method has been developed for the determination of these three elements when present together as thiocyanates extracted in acetone [77]. The thiocyanate complex of Co (II) has a maximum absorption at 625 mμ, that of Cu at 380 mμ and that of Fe (III) at 480 mμ. Since the color of the Cu thiocyanate complex is very unstable it is proposed that a small amount of oxidizing agent be added to stabilize it in solution. Methods are also adduced for eliminating the effects of some other cations and anions.

The accuracy of the determination of these elements is low. For a content of Co and Cu >50 mg and of iron >5 mg the accuracy is ca. 10% relative units.

The number of elements determined spectrophotometrically increases continuosly. It is impossible in this brief review to enumerate all the applications of the spectrophotometer; nevertheless from what has been said it is possible to get an idea of the potentialities of the method, particularly for the determination of three components in solution.

EXPERIMENTAL

It was our intention in this investigation to develop a spectrophotometric method for the determination of vanadium and titanium when present together, using the yellow color of ammonium vanadate in sulfuric acid solution, and the blue color of vanadium (IV) solution in sulfuric acid for the determination of vanadium, and the color of the complex formed between titanium and chromotropic acid for titanium. We therefore studied the absorption spectra of the solutions indicated and the effect of a number of factors on the absorption.

It should be noted that the absorption spectra of vanadium (III) and (IV) have been studied in solutions of perchloric and hydrochloric acids respectively for constant ionic strengths of the solution. Basically, however, this investigation was devoted to the absorption spectra of vanadium (III) in order to establish the nature of the hydrolysis product of vanadium (III) - (VOH^{2+}) [78].

All measurements were made on the SF-11 photoelectric spectrophotometer using; cells with a 1 cm layer thickness.

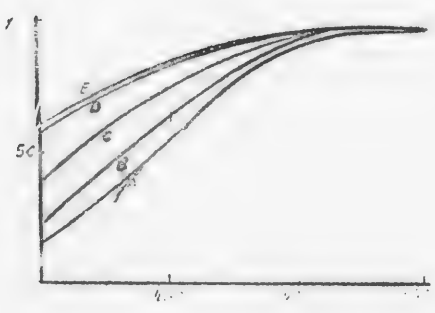


Fig. 4. Transmission curves of NH_4VO_3 for various vanadium concentrations. All solutions were 0.8 N with respect to H_2SO_4. A) 4 mg V. B) 3 mg, C) 2 mg and D) E-1 mg V per ml.

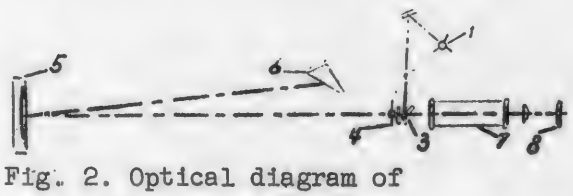


Fig. 2. Optical diagram of spectrophotometer SF-11.

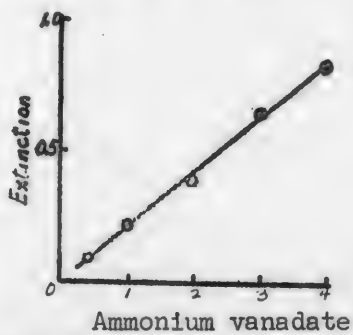


Fig. 5. Curve relating extinction to ammonium vanadate concentration; λ = 400 mμ.

Ammonium metavandate in 0.8 N H_2SO_4 was used as the original substance for the vanadium (V) and (IV) solutions. Contemporary theory of the structure of vanadium (V) compounds in acid media represent vanadium (V) in the form of a complex cation, which determines the bright yellow color of its solutions [79] Solutions of vanadium (IV) of a blue color are obtained by reduction of NH_4VO_3 by means of sodium sulfite or lactic acid with heating. For the color reactions of V (IV) vide [80]. Chromotropic acid, proposed by Tananaev and Panchenko for the qualitative determination of Ti and subsequently used for the quantitative determination of Ti in steel and cast iron [81], was used as the reagent for Ti. The titanium sulfate solution was prepared by treating $K_2TiF_2 \cdot H_2O$ with concentrated H_2SO_4, with subsequent solution of the titanium sulfate in 5% H_2SO_4.

Chromotropic acid was used in the form of a 6% aqueous solution. A few small crystals of Na_2SO_3 were added to improve the stability of the chromotropic acid solution.

Absorption Spectra of Vanadium (V) and (IV)

In order to determine the transmission spectra of vanadium (V), solutions of ammonium metavanadate with varying contents of V in 0.8 N H_2SO_4 were prepared. The transmission spectra of these solutions in the wave length ranges 400 - 1000 mμ and 300 - 1000 mμ are adduced in Fig. 4. These curves show that vanadium (V) has a maximum absorption in the visible spectrum at 335 mμ.

The form of the curves (Fig. 4) is independent of the vanadium concentration. On addition to the vanadium (V) solution of a small amount of titanium as the sulfate no significant change in the value of the vanadium transmission was observed through the whole wave length range studied (Curve D, Fig. 4). In order to check the validity of Beer's law for vanadium (V) a series of solutions was prepared with concentrations of vanadium ranging from 0 - 4 mg/ml in 0.8 N H_2SO_4. The extinction and vanadium concentration is illustrated in Fig. 5.

It is evident from Fig. 5 that a straight line is obtained for the concentration range 0.4 - 4 mg/ml V; all the experimental points lie very close to this line. For a layer thickness of 1 cm, 0.04 mg V/ml is the limiting sensitivity of this spectrophotometric determination of vanadium (V). A study of the effect of the acidity on the extinction of vanadium (V) at 500 mμ showed that changes in acidity from 0.4 N to 4 N H_2SO_4 has practically no effect on the extinction of the vanadium (V) solution.

It follows from these results that vanadium can be determined spectrophotometrically by the color of the vanadium (V) solution in sulfuric acid solutions from 0.4 to 4 N.

The transmission spectra of vanadium (IV) were taken in the wave length region 300 - 1000 mμ. The transmission spectra of solutions of vanadium (IV) in 0.8 N H_2SO_4 obtained by reduction of vanadium (V) with lactic acid on heating are given in Fig. 6, together with that of the lactic acid alone at the same concentration as that used with the vanadium solutions. From Fig. 6 it is evident that vanadium (IV) gives two transmission minima at 325 mμ and 750 mμ respectively. Similar transmission spectra are given by vanadium (IV) solution obtained by reduction of vanadium (V) with sodium sulfite. Curve D, Fig. 6 represents the transmission of lactic acid on its own; this has only one minimum at 330 mμ. For the determination of vanadium therefore the wave length of the second minima was used, i.e., the 750 mμ one. At this wave length the absorption of series of vanadium (IV) solutions in 0.8 N H_2SO_4 was measured; the concentration of the vanadium varied from 0.1 to 2 mg/ml. Extinction is plotted against vanadium concentration in Fig. 7, from which it is clear that all the experimental points lie on one straight line for the concentrations indicated.

Consequently the color of vanadium (IV) solutions follows Beer's law for a wide concentration range of vanadium. The sensitivity of the determination

of vanadium (IV) was found to be 0.01 mg V/ml for a layer thickness of 1 cm.

On investigating the effect of the acidity of the solution (with respect to H_2SO_4) on the estimation of vanadium, it was found that it has no effect over a wide range; nevertheless at low pH's (pH 2 - 3) the reduction of vanadium (V) to vanadium (IV) is not quantitative. Titanium does not affect the extinction of vanadium (IV) solution at 750 mμ. Neither does Fe^{3+} interfere, since it is reduced to Fe^{2+} by the sulfite. Thus vanadium can be determined spectrophotometrically by measuring the absorption of vanadium (IV) solutions. The determination of vanadium by the color of vanadium (IV) is more sensitive than by the yellow color of vanadium (V).

Absorption Spectra of the Complex Formed Between Titanium and Chromotropic Acid

In order to study the absorption of the Ti-chromotropic acid complex a solution of pH 2 was prepared containing 0.05 mg Ti [as $Ti(SO_4)_2$] and 0.5 ml chromotropic acid (6%) in 25 ml.

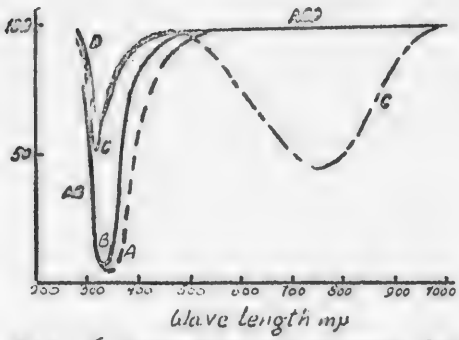


Fig. 6. Transmission curves for vanadium solutions (V), (IV); (V) +Ti (IV) and lactic acid.
A - NH_4VO_3+$Ti(SO_4)_2$ (0.4 mg V and Ti/ml; B - NH_4VO_3 (0.4 mg V/ml); C - VO^{2+}; D - lactic acid. All solutions in 0.8 N H_2SO_4.

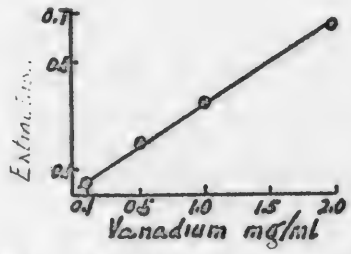


Fig. 7 Relation between extinction and vanadium (IV) concentration.

The adsorption of the solution was measured in the range 300 - 1000 mμ. In addition the adsorption spectra of a 6% chromotropic acid solution was taken (Fig.8).

Fig. 8 shows that the titanium-chromotropic acid complex has two transmission minima. The first is near the ultraviolet region at 350 mμ and belongs to the chromotropic acid (Curve A); the second at 475 mμ belongs to the complex. Determination of the transmission of the titanium complex should therefore be made at 475 mμ. If this value is compared with the wave length at which the transmission minimum of vanadium is obtained, i.e, 750 mμ, then it is clear that the determination of these elements when they are present together is comparatively simple. Subsequently measurements of the transmission of solutions of the titanium complex were made at different values of the acidity (with respect to H_2SO_4), Fig.9. From Fig. 9 it is clear that the acidity has considerable influence on the transmission of the complex; this is in agreement with Babko [86] and Generozov's results. The transmission increases considerably in going from 0.01 to 0.05 N H_2SO_4. In practice, therefore, in order to get the optimum color developed, the acidity of the titanium solutions should be adjusted to concentrations not greater than 0.01 N, since for lower acidities, changes in the transmission of the titanium complex do not occur. Therefore all further measurements were made with titanium solutions 0.01 N with respect to H_2SO_4.

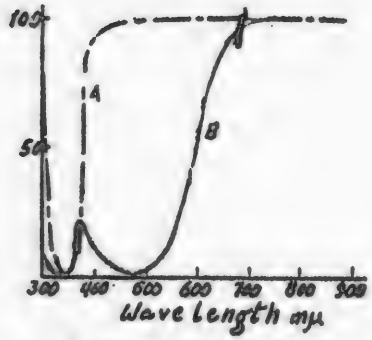


Fig. 8. Transmission curves for chromotropic acid and for the complex of titanium with chromotropic acid.
A - Chromotropic acid, B - complex of titanium and chromotropic acid.

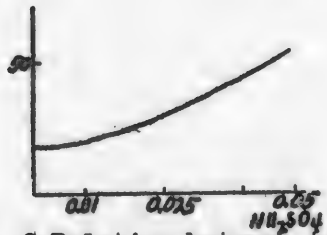


Fig. 9. Relation between transmission of the titanium-chromotropic acid complex and the acidity; λ = 475 mμ.

The effect of the amount of chromotropic acid was also investigated. On Fig. 10 the relation is given between transmission and chromotropic acid concentration for a constant amount of titanium (0.1 mg in 25 ml) at 475 mμ. This curve shows that the amount of chromotropic acid (within the range 0.5 - 2 ml) has very little effect on the transmission of the titanium complex). In all subsequent experiments therefore the amount of chromotropic acid added was kept at 0.5 ml.

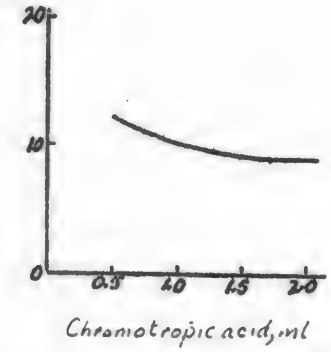


Fig. 10. Relation between transmission and amount of chromotropic acid.

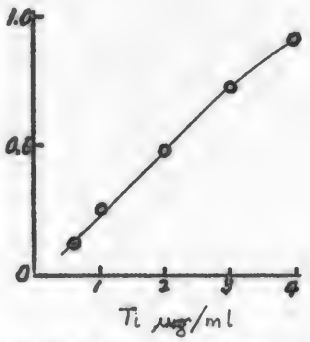


Fig. 11. Relation between the transmission of the complex formed between titanium and chromotropic acid and the acidity; λ = 475 mμ.

The color stability of the titanium complex was also investigated. It was found that even on long standing (48 hours) no change in the transmission of solutions of the complex occurred. A series of experiments was then carried out in which solutions were prepared with concentrations of titanium varying from 0.5 to 4 μg/ml in 0.01 N H_2SO_4 to which 0.5 ml of chromotropic acid solution was added. Extinction was measured at 475 mμ. The relation between extinction and titanium concentrations in solution is plotted in Fig. 11. All the experimental points lie on one straight line, which shows that the color of the titanium complex follows Beer's law.

Spectrophotometric Determination of Vanadium and Titanium When They Occur Together

In order to estimate the accuracy of the determination of vanadium and titanium when present together, solutions containing various ratios of the metals were prepared in 0.01 N H_2SO_4. One series of these solutions contained titanium sulfate and ammonium vanadate and their absorption was measured directly at 475 mμ after addition of 0.5 ml chromotropic acid and making up to a volume of 25 ml in order to determine the titanium.

In another series of solutions containing titanium sulfate and ammonium vanadate, a known excess of sulfuric acid was added before addition of the chromotropic acid; the whole was then adjusted with ammonia or NaOH to a pH of 2.

The third series of measurements was made after reduction of the vanadium by means of Na_2SO_3 or lactic acid. In order to do this a mixture of ammonium vanadate and titanium sulfate was made, the pH of the solution adjusted to 2, and a few small crystals of sodium sulfite or 1 ml lactic acid added. On heating for a few minutes the vanadium (V) is reduced to vanadium (IV). When this was done it was found that the solutions obtained were colored green and not blue, indicating an incomplete reduction of the vanadium (V) because of the low acidity of the solution. Actually on addition of a large excess of acid to the solution the reduction of vanadium (V) proceeds quantitatively. However, high acidity of the solution interferes with the development of the colored complex of titanium and chromotropic acid. We therefore adopted the following procedure after reduction of vanadium (V) in a solution whose acidity is high enough: the solution was transferred to a 10 ml standard flask and made up to the mark with distilled water. An aliquot of the solution was measured into a 25 ml flask, water added to bring the volume up to 20-23 ml, the pH adjusted to 2 by addition of ammonia and finally 0.5 ml chromotropic acid solution added and the volume made up to the mark. The absorption of this solution was measured at 475 mμ (for determination of the titanium) and at 750 mμ for the determination of vanadium). However, since at low concentrations of vanadium its determination in a cell with only a 1 cm layer is not sufficiently sensitive, it was determined by the absorption of the blue color formed before addition of the chromotropic acid at 750 mμ or by means of a cell with a greater layer thickness.

From Table 2 it is clear that for the determination of titanium in the presence of a large excess of vanadium (V) but without neutralization of excess acid the results are completely satisfactory even for low concentrations of titanium (Experiments 1 - 5). Mean error- 3% relative.

On introducing excess sulfuric acid with subsequent neutralization and adjustment of the pH to 2, the deviation of the titanium becomes considerable (20 - 30%) on the high side (Experiments 6 - 9), since in this case a color is superimposed which arises from the conversion of the vanadium (V) ion into a more complex ion. When titanium is determined with chromotropic acid in the presence of vanadium (IV) the results obtained are somewhat high, since the vanadium exhibits a certain amount of absorption at 475 mμ. The mean deviation is 5%. For more accurate measurements this factor must be taken into account.

In the case of vanadium satisfactory results can be obtained by measuring the absorption of vanadium (IV) solutions. The mean error in this case amounts to 5%.

As a result of this investigation the following analytical procedure is tentatively suggested for the determination of titanium and vanadium when present together; after separation of Ti and V as normally recommended [83], the solution containing both elements is made up to a known volume A. An aliquot is taken and diluted so that the normality of the acid used is ca. 0.01 N, when chromotropic acid is added and the solution made up to a standard volume B. The colored solution formed is then placed in the cell and its absorption at 475 mμ measured. From a calibration curve constructed beforehand the Ti content is then determined. When the solution is strongly acid it is reduced with Na_2SO_3 with heating, made up to a definite volume and aliquots taken. The pH of the aliquots is adjusted to 2 by

TABLE 2

Test No.	V taken, mg	Ti taken, mg	V found, mg	Ti found, mg	Difference, mg		Error, %		Observations
					V	Ti	V	Ti	
1	0.50	0.050	–	0.053	–	+0.003	–	+6.0	V introduced as NH_4NO_3, Ti as the sulfate, 0.01 N H_2SO_4. Chromotropic acid added and volume made up to 25 ml.
2	0.50	0.075	–	0.076	–	+0.001	–	+1.3	
3	0.25	0.050	–	0.052	–	+0.002	–	+4.0	
4	0.10	0.050	–	0.051	–	+0.001	–	+2.0	
5	0.75	0.090	–	0.092	–	+0.002	–	+2.3	
							Mean	3.12	
6	1.00	0.075	–	0.091	–	+0.016	–	+21.0	Conditions as above, but excess acid neutralized with NH_4OH.
7	1.00	0.075	–	0.086	–	+0.009	–	+12.0	
8	1.50	0.075	–	0.090	–	+0.015	–	+20.0	
9	1.00	0.250	–	0.250	–	–	–	–	In Experiments 10, 11, and 12, Ti and V are determined together after adjustment of the acidity to 0.01 N and addition of chromotropic acid.
10	2.50	1.000	2.30	1.000	-0.2	–	-8.0	–	
11	2.50	0.050	2.30	0.052	-0.2	+0.002	-8.0	+4.0	
12	1.50	0.025	12.50	0.023	–	-0.002	–	-8.0	
13	5.00	0.200	4.80	–	-0.2	–	-4.0	–	In Experiments 13, 14, and 15, Ti is determined in the mixture, V by the blue color.
14	5.00	0.100	4.80	–	-0.2	–	-4.0	–	
15	2.50	0.90	2.30	0.925	-0.2	+0.025	-8.0	+2.7	
16	2.50	0.90	–	0.937	–	+0.037	–	+4.11	Only Ti determined after reduction of V, neutralization of the solution and addition of chromotropic acid.
17	2.50	0.90	–	0.937	–	+0.037	–	+4.11	
						Mean	-5.3	±4.98	

means of NH_4OH and chromotropic acid added, the volume is then finally made up to a standard volume and the titanium determined at 475 mμ. Vanadium is determined in the solution obtained directly after reduction with Na_2SO_3 (i.e., before neutralization with NH_4OH, etc.), by measurement of its absorption at 750 mμ. The vanadium content is determined by means of a calibration curve constructed beforehand.

In conclusion we should like to express our thanks to A.P.Vinogradov, Corresponding Member of the Academy of Sciences, for his suggestion for compiling this report and for his interest in the work.

We also wish to thank G.I.Ostrozhenskaya, who kindly gave us the chromotropic acid.

SUMMARY

1. A short review is given of literature relating to use of the spectrophotometric method in various branches of chemistry during the last 4-5 years.

2. The absorption spectra of vanadium (V) and vanadium (IV) in acid solution and of the complex formed between titanium and chromotropic acid have been examined.

3. The effect of various factors (pH, amount of reagent, time of standing, etc.) on the value of the extinction of the complex of titanium and chromotropic acid, and also on the extinction of vanadium solutions, has been investigated.

4. A spectrophotometric method for the determination of vanadium and titanium when present together has been suggested. Vanadium is determined as vanadium (V) at 400 mμ or as vanadium (IV) at 750 mμ. Titanium is determined with chromotropic acid at 475 mμ in the presence of vanadium (IV).

LITERATURE CITED

[1] I.P.Alimarin, "Photoelectric Colorimeters with Selenium Photoelements, and Their Use in Chemical Analysis", State Geol. Press, 1944.

[2] V.M.Chulanovsky , "Introduction to Molecular Spectral Analysis", 1950.

[3] A.K.Babko, and A.T.Pilipenko, "Colorimetric Analysis", State Chem. Press, 1951.

[4] A.M.Terenin, "The Photochemistry of Dyes", USSR Acad.Sci.Press, 1947.

[5] Kirk, "Quantitative Ultra-microanalysis", Edited by I.P.Almarin, 1952.

[6] A.K.Babko, Factory Labs., 13, 9 (1947).

[7] V.I.Kuznetsov, J. Gen. Chem. 20, 807, 816 (1950).[1)]

[8] G.H.Ayres and A.S.Meyer, Anal. Chem. 23, 299 (1951).

[9] M.G.Mellon, Analytical Absorption Spectroscopy, 1950.

[10] M.V.Savostyanova, Bull. Acad. Sci.USSR, Ser.Phys., 11, 424 (1947).

[11] V.V.Perekalin and M.V.Savostyanova, J. Gen. Chem. 21, 1329 (1951).[2)]

[12] V.V.Perekalin and M.V.Savostyanova, and P.I.Morozova, Bull. Acad. Sci. USSR, Ser. Phys., 14, 527 (1950); J.Gen.Chem., 22, 821 (1952).[3)]

[13] N.A.Valyashko and Yu.S Rozum, J. Gen. Chem. 17, 755, 783 (1947).

[14] N.A.Valyashko and A.E.Lutskin, J. Gen. Chem. 21, 939, 1069, 1091 (1951).[4)]

[15] A.E.Lutsky, J. Gen. Chem. 20, 749 (1950).[5)]

[16] N.A.Valyashko and I.T.Depeshko J. Gen. Chem. 20, 479 (1950).[6)]

[17] M.I.Plekhan and N.I.Gavrilov, J. Gen. Chem. 18, 1843 (1948).

[18] N.A.Poddubnaya and N.I.Gavrilov, J. Gen. Chem. 18, 1848, 1860 (1948).

[19] M.I.Plekhan, J. Gen. Chem. 21, 312, 316, 574, 579 (1951).[7)]

[20] M.I.Plekhan and A.M.Kan, J. Gen. Chem. 20, 2105 (1950).[8)]

[21] A.Lagafonova, J. Gen. Chem. 17, 1055 (1947).

[22] M.F.Ivanova, J. Anal. Chem. 2, 219 (1947).

[23] K.V.Flerov and B.V.Ozimov, J. Gen. Chem. 20, 789 (1950).[9)]

[24] M.S.Barvinok, J. Gen. Chem. 19, 612, 793, 1028 (1949); 20, 1947, (1950); 21, 1207 (1951).[10)]

[25] A.K.Babko, J. Gen. Chem. 17, 443 (1947).

[26] S.E.Turner , R.C Anderson, J. Am. Chem. Soc. 71, 912 (1949).

[27] L.S.Lilich, J. Gen. Chem., 22, 730 (1952).[11)]

[28] I.M.Korenman and A.M.Fisher, Factory Labs., 14, 1058 (1948).

[29] L.I.Belenky and M.E.Kazantseva, Factory Labs., 18, 278, (1952).

[30] Th.N.Burbridge, Ch.H.Hineu, A.F.Schick, J. Labor.a Clin. Med. 35, 983 (1950).

[31] R.I.Veksler, J. Anal. Chem. 4, 14, (1949); 1, 301 (1946).
[32] Y.C.Speck, Anal. Chem. 20, 647 (1948).
[33] O.D.Shreve and M.R.Heetner, Anal. Chem. 23, 441 (1951).
[34] W.T.Haskinsa, G.W.Luttermoser, Anal. Chem. 23, 456(1951).
[35] Fr.F.Hazllett, R.B.Hannan, Y.H.Wells, Anal. Chem. 22, 1132 (1950).
[36] D.C.Karpenter, Anal. Chem. 20, 536 (1948).
[37] C.O.Willits, M.L.Swain, W.A.Connelly, B.A.Brice, Anal. Chem. 22, 430 (1950).
[38] E.Y.Center, R.R. MacIntosh, Ind. Eng. Chem. Anal. Ed. 17, 239 (1945).
[39] R.A.Dunleavy, S.E.Wiberley, J.H.Harley, Anal. Chem. 22, 170 (1950).
[40] J.P.Mehlig, M.J.Stepherd, Anal. Chem. 21, 642 (1949).
[41] M.S.Pepi, Anal. Chem. 22, 560 (1950).
[42] H.V.Meek, Ch. 7. Banks, Anal. Chem. 22, 1512 (1950).
[43] P.V.Mervel, J. Anal. Chem., 2, 103 (1947).
[44] H.K.Kuskova, J. Anal. Chem. 2, 7 (1947).
[45] S.E.Wiberley, L.G.Basset, Anal. Chem. 21, 609 (1949).
[46] L.Silverman, Anal. Chem. 20, 906 (1948).
[47] H.Irving, E.Y.Ridson, G.Andrew, J. Chem. Soc. 1949, 537.
[48] R.C.Fergusson, C.W.Bancks, Anal.Chem. 23, 1486 (1951).
[49] R.C.Fergusson, C.W.Bancks, Anal. Chem. 23, 448 (1951).
[50] R.G.Keenan B.M.Flick, Anal. Chem. 20, 1238 (1948).
[51] D.P.Malyuga, J. Anal. Chem. 1, 176 (1946).
[52] A.P.Vinogradov, Proc. Acad. Sci. USSR, A, 249 (1931).
[53] M.D.Cooper, P.R.Winter, Anal. Chem. 21, 605 (1949).
[54] G.Telep, D.F.Boltz, Anal. Chem. 23, 901 (1951).
[55] G.H.Ayres, B.L.Tuffly, Anal. Chem. 23, 304 (1951).
[56] L.M.Kulberg, M.L.Derbaremdiker, Factory Labs., 13, 1488 (1947).
[57] R.A.Johnson, F.P.Kwan, Anal. Chem. 23, 651 (1951).
[58] Moeller, Brantly, Anal. Chem. 22, 433 (1950); A.W.Wylie, J. Soc. Chem., Ind. 69 143 (1950).
[59] J.A.Wybrew, G.Matrone, H.M.Baxley, Anal. Chem. 20, 759 (1948).
[60] E.D.Marshall, R.R.Rickard, Anal. Chem. 22, 795 (1950).
[61] G.H.Ayres, W.N.Wells, Anal. Chem.22, 317 (1950).
[62] G.H.Ayres, F.Young, Anal. Chem. 24, 165 (1952).
[63] D.F.Boltz, M.G.Mellon, Anal. Chem. 20, 749 (1948).
[64] A.Dolance, P.W.Healy, Ind. Eng. Chem., Anal. Ed. 17, 718 (1945).
[65] C.D.Anselm, R.Y.Robinson, J. Marine Research 10, 203 (1951).
[66] W.G.Gross, L.K.Wood, McHargue, Anal. Chem. 20, 900 (1948).
[67] J.K.Fogo, M.Popowsky, Anal. Chem. 21, 732 (1949).
[68] A.E.Uspensky, Proc. Inst. Chem. Reagents 1927, No. 4 1935.

[69] V.F.Maltsev and A.L.Davydov, Factory Labs. 13, 926 (1947).

[70] J.J.Linganeand J.W.Collat, Anal. Chem. 22, 166 (1950).

[71] R.Bastian, R.Weberling, F.Palilla, Anal. Chem. 22, 160 (1950).

[72] E.W.Martin, A.N.Hixson, W.M.McNabb., Anal. Chem. 20, 1043 (1948).

[73] G.V.Potter, C.E.Armstrong, Anal. Chem. 20, 1208 (1948).

[74] W.H.Davenport, Anal. Chem. 21, 710 (1949).

[75] I.Geld, J. Carrol, Anal. Chem., 21, 1098 (1949).

[76] A.Weissler, Ind. Eng. Chem., Anal. Ed. 17, 695 (1945).

[77] R.E.Kitson, Anal. Chem. 22, 664 (1950).

[78] S.C.Furman, C.S.Garner, J.Am. Chem. Soc. 72, 1785 (1950).

[79] V.S.Syrokomsky and Yu.V.Klimenko,"Vanadometry", 1950.

[80] V.I.Kuznetsov, Proc. Acad. Sci. USSR, 39 (1946).

[81] R.Guenther R.H.Gale, Anal. Chem. 22, 1510 (1950).

[82] G.A.Panchenko and M.V.Bietsky, J. Appl. Chem. 8, 720 (1935).

[83] S.M.Luchin, Proc. Acad. Sci.USSR, 49, 6 (1945)

[84] V.M.Chulanovsky, A.F.Adrianov and B.I.Rubinovich, J. Anal. Chem. 4, 345 (1949).

[85] N.P.Komar, Proc. Institute Ferrous Met., Acad. Ukrain S.S.R. 1, 120 (1946).

[86] A.K.Babko, Factory Labs. 13, 645 (1947).

[87] A.K.Babko and M.M.Korsun, Factory Labs. 14, 1160 (1948).

[88] N.P.Komar, J. Anal. Chem. 5, 139 (1950).

Received October 17, 1952

---

1) See Consultants Bureau translation, p.845, 853.

2) See Consultants Bureau translation, p.1451.

3) See Consultants Bureau translation, p.853.

4) See Consultants Bureau translation, p.1029, 1171, 1193.

5) See Consultants Bureau translation, p.787.

6) See Consultants Bureau translation, p.513.

7) See Consultants Bureau translation, p.341, 347, 635, 641.

8) See Consultants Bureau translation, p.2181.

9) See Consultants Bureau translation, p.829.

10) See Consultants Bureau translation, p. 563, 775, 1019; 2015; 1315.

11) See Consultants Bureau translation, p. 795.

QUANTITATIVE X-RAY SPECTROGRAPHIC ANALYSIS

V.V.Vainshtein, I.D.Shevaleevsky, and M.M.Kakhana

(V.I.Vernadsky Institute of Geochemistry and
Analytical Chemistry, Acad. Sci. USSR, Moscow)

Quantitative X-ray spectrographic analysis is based on a comparison of the intensity of the X-ray lines of the test sample and of a standard respectively, under identical, standard conditions, The intensity of these lines, all other conditions being equal, is proportional to the number of atoms of each element in the test sample. However, when a photographic method is employed for registering the spectra it is not the intensity of the lines but the corresponding blackening that is compared. The latter depends on the intensity in a non-linear manner, as a result of which many difficulties crop up in practical analytical X-ray spectroscopy. This non-linear relation is also the source of the largest analytical errors. One of the first attempts to overcome the difficulties encountered in X-ray spectrographic analysis arising out of this non-linearity between the intensity of a line and the corresponding blackening was made by Hevesy, who in conjunction with a number of his coworkers proposed a method conveniently called "the null method". This method consists essentially in adding to the test substance an amount of a standard element such that the blackening of the lines being compared becomes identical. This quantitative method of analysis became widely known and was included in all textbooks on X-ray spectrography [1, 2]. It was by means of this method that most of the early investigations in X-ray spectrographic analysis were carried out [3, 4, 5]. However,as the method came to be more and more widely used some of the fundamental drawbacks of Hevesy's method became evident, these drawbacks were connected with the necessity of repeating the analysis several times, and choosing the amount of standard element to be added to the test mixtures for equalizing the blackening of the lines being compared. This leads, apart from a considerable waste of time in production analysis, to an increase in the amount of substance necessary for analysis, and finally requires a large selection of standard elements. What has been said above shows that this method is not suitable for use under factory conditions, where the speed of analysis is nowadays of decisive importance. That is why investigators were often compelled with a corresponding sacrifice of accuracy to depart from strict observance of Hevesy and his successors recommendations and used for quantitative analysis lines with unequal blackening or separated from each other by distances in excess of the usually recommended 100 XU. Some authors when carrying out analysis in this way [6, 7] preferred to use a "blackening curve", experimentally constructed beforehand, others [8] carried out analysis by means of a series of calibration curves, implicitly including the relation between blackening and the intensity for a selected type of photographic material. In some special cases it is possible to carry out an analysis with sufficient accuracy on the assumption that the blackening of a line is, within narrow limits, proportional to the intensity.

Despite the apparent differences between the analytical methods mentioned above, which to various degrees enable them to be used for the solution of some particular practical problem, they all have a large number of coarse errors in common; firstly, the accuracy of these methods of analysis is less than the accuracy of Hevesy's "null method"; secondly they can only be used when the experimental conditions under which the fundamental calibration curve was obtained are very strictly controlled; such as strict standardization of the photographic

material, standard conditions of developing the spectrogram, the successful choice of exposure time during which the spectral lines under observation are located in the necessary blackening region, etc.. Non-observance even of only one of these factors immediately leads to a decrease in the accuracy of the analysis. Thus, although the drawbacks of the methods described are often worth the possibility of carrying out an analysis of a large number of elements rapidly, nevertheless the search for new analytical methods which ensure the necessary rapidity and accuracy of an analysis remains a practical problem.

During the last two years a number of investigations have been carried out which had as their aim the development and comparative testing of new methods of X-ray spectrographic analysis.

Some of the results of this work are given in the present article.

Use of the Form of the Spectral Lines for X-ray chemical analysis

It is known that [9] the form of a large group of X-ray lines of the elements remains practically unchanged when the atoms of these elements enter into the composition of chemical compounds, and does not depend on the aggregate state of the substance. Finally the form of the lines does not depend on their intensity. It was shown e.g., that the form of the $K\alpha_{1,2}$ line of elements, the atomic number of which is greater than or equal to 30, is closely described by the dispersion formula

$$I = \frac{I_0 \left(\frac{\Gamma}{2}\right)^2}{(\nu - \nu_0)^2 + \left(\frac{\Gamma}{2}\right)^2}, \qquad (1)$$

where I – is the intensity of a point on the contour of a line at a distance $(\nu - \nu_0)$ from the frequency corresponding to the maximum; I_0 – the maximum intensity of the line at the point $\nu = \nu_0$; while Γ – is a constant numerically equal to the width of the emission line at a height equal to half its intensity.

This means that if each point on the contour of the spectral line is characterized by a quantity n (either whole or fractional), which indicates how many times the intensity of the line at its maximum is greater than that at a given point on its contour, (i.e., making $n = I_0/I$), then a knowledge of the value of Γ will enable the width of the line at any section of it (x) to be calculated [9] accurately according to the formula (2)

$$x = \Gamma \sqrt{n - 1}. \qquad (2)$$

It is evident that the relation (2) will be valid for any given line independently of its intensity. Consequently it can be used [9] both for the direct study of the form of the X-ray emission line, and for the solution of the reverse problem, finding the value of n on the basis of given measurements of the width of the line at an arbitrary point on its contour and of the value of Γ.

By means of (2) it is possible to calculate the relative intensities of two or more lines (the form of which is described by a dispersion formula) if the values of Γ are known for each of them and the widths are measured at any arbitrary section, which is however the same for all the lines compared. In particular, if a point were found on the contour of one of the lines (considered as the standard line) the intensity of which were identical with the intensity of the peak of another line, located side by side with the first, the value of n, calculated for this point would be equal to the ratio of the intensities of these two lines. Thus, by measurements of the width of the lines of a series of standard elements and using formula (2) the basic problem of X-ray spectral analysis can be solved in a different way from those adopted previously. What has been said above is the basis

of the new method of quantitative spectrographic analysis. It can be carried out in practice by two methods. The first of these which is essentially completely analogous to Hevesy's "null method" was first proposed in 1937 [10] and as further tests have shown [11, 12, 13] can be used both in optical and X-ray spectroscopes. The second method was proposed and tested fairly recently [14].

Both methods are based on the fact that the true form of a line in the intensity scale after its registration of a photographic plate (traced out on the blackening scale) changes in such a way that the distance between points of equal intensity remains strictly unchanged. This characteristic of the law of the transformation of the curve into another enables the relative intensity of a point on the contour of a line registered on the blackening scale to be calculated directly using (2) without having to reconvert from the blackening scale to the intensity scale for the curve as a whole.

In the first of these methods of analysis mentioned above the use of the blackening curve is excluded completely, since the width of a standard line at a height equal to the blackening of the line of the test element (used for calculations of the relative intensity of both lines) does not depend on the form of the curve $S = S(I)$.

In the second method, on the other hand the regular change in intensity along the contour of the line together with the invariance mentioned above of the distance between points of equal intensity relative to transformation from the blackening scale to the intensity scale, is used for constructing the characteristic curve of the emulsion, by means of which the analysis is subsequently carried out.

The values which are used as the original series of intensities in the method described for constructing the blackening curve are those which correspond to individual points on the contour of the X-ray spectral lines which are related to each other by the dispersion law. When the true profile of a line is registered on an X-ray plate it will be transformed into another profile because of the non-linear relation between blackening and intensity. The law which governs this transformation can be found experimentally, if the property mentioned above is used viz., that on transforming one curve into the other, two symmetrical points on their contour (corresponding to one value of blackening of intensity) remain equidistant. In this way, having measured the width of the line at any cross-section of the experimental profile (on the blackening scale), relation (2) can be used and the value of I/I_0 corresponding to a given blackening value on the true profile of the line (on the intensity scale) found.

The use of formula (2) presumes a knowledge of Γ[1]. In the absence of deformations of the profile of the line brought about by the spectrogram itself, this quantity is an atomic constant equal to the sum of the widths of the initial and final levels for an electron transfer in the emmitting atom. When working with a focussing spectrograph with a bent crystal the value of Γ differs to varying extents from the natural width of the spectral line and should be considered as a constant which is dependent on the characteristics of the apparatus used. The difference between this quantity and the true value of $_{true}$ is particularly great when working with a Johann type of spectrograph where $(\Gamma - \Gamma_{true})$ depends on the cotangent of the angle of reflection and in some cases can exceed the natural width of the line by 2-3 times. It is essential that all this be borne in mind when attempting to use these types of apparatus for carrying out sensitive physical invest-

---

1) The case where the values of Γ for two lines being compared are equal is an exception. In this case having measured the width of the two lines at an arbitrary but identical cross section of the two lines, it is possible to calculate the relative intensity, not knowing Γ by using the relation $\frac{I_1}{I_2} = \frac{\left(\frac{x_1}{x_2}\right)^2 + (k - 1)}{k}$

where k is a quantity which depends on n_2, and has a value which is practically constant at $\sim 1.12 \pm 0.02$ for $8 < n_2 < 11$.

igations. When working with an analytical method (in the case where the form of the lines registered does not undergo assymetrical distortions) it is important only to indicate a reliable method for the experimental determination of Γ, in which the latter is considered to be related to the apparatus constant and numerically equal to the width of a line at half the intensity of its maximum.

If during an analysis it is possible to use the $K\alpha_1$ line of any element as the standard, then finding is a simple elementary problem. Since the ratio of the intensities of the $K\alpha_1$ and $K\alpha_2$ lines of all elements are equal to or very nearly 0.5 (i.e., $\underline{n} = 2$) then it follows from formula (2) that the value of Γ for the $K\alpha_1$ line for any form of the relation $S = S(I)$ and for any absolute value of the blackening of the $K\alpha_1$ line should be equal to its width measured at the peak height of the $K\alpha_2$ line of the element.

Similarily the width of the $L\alpha_1$ line measured at the height of the peak of the $I\alpha_{2,1}$ line should amount to $2.85\ \Gamma$ [1]. In the general case (e.g., when using a singlet line as the standard line) the half width of the line Γ can be determined by two methods. According to the first method, a part of the line is artificially weakened by means of aluminum foil of a known density. Having subsequently measured the width of the unweakened part of the line at the peak height of the blackening of its weakened part, Γ is calculated by formula (2). In practice the second method is particularly suitable, in this method side by side with the test line, the $K_{\alpha 1,2}$ doublet of another element (the standard) is photographed. The amount of the standard element in the specially prepared mixture is chosen so that the blackening of the $K_{\alpha 1}$ line on the X-ray spectrogram is equal to or near to the blackening of the test line.

Under these conditions the half width of this line Γ can be determined directly by measuring the width at the height of maximum blackening of the $K\alpha_2$ line of the standard element.

It was shown experimentally that the basis of this analytical method described is fundamentally sound. In a series of tests the conclusions concerning the dispersion form of the X-Ray $K\alpha_{1,2}$ lines of elements with atomic numbers greater than or equal to 30 were again confirmed, and the constancy of the value of Γ as measured by one of the methods described above proved for a wide range of blackening of the lines and a wide range of spectrogram backgrounds. A consideration of the experimental results enables us to affirm that despite a ten-fold change in blackening of the lines and background of the spectrogram the values of Γ characterizing each of the emission lines considered, remain constant with a mean error of 3%. Similarily the width of the $L\alpha_1$ line measured at the peak height of the $L\alpha_2$ line remains constant. The half width calculated by means of these measurements is in good agreement with the value obtained by direct calculation of the profile of the curves for true intensities.

In order that the results may be more general and independent of the thickness and the degree of uniformity of the photographic emulsion it is expedient to use one-layer films.

Since the change in width of the precision slit of the photometer within the limits 0.2 - 0.5 mm does not (as control test showed) affect the results, it is better to give them preference over wider slits; their use ensures that the photometric results are practically independent of the irregularity of the distribution of the emulsion grains of the photographic film. We used a slit width of 0.4 mm for an increase of 20 times in the photometer.

When working with focussing X-ray spectrographs the accuracy and reliability of quantitative X-ray spectral analysis which is based on measurements of the form

---

[1] It is assumed that the ratio of the intensities of the lines is equal to 0.11.

and width of the X-Ray spectral lines, to a large extent depends on the constancy of these parameters along its length. It has been shown that during the bending of the crystal in the spectrograph by means of a method proposed by Vainshtein, Narbutt and Gilvarg [15], the width of the line at the focus of the apparatus remains practically constant along several tens of millimeters of its length. Apparently similarily close results can be obtained when using another of the methods proposed for bending crystals in X-ray spectrographs [16, 17, 18] or by its simplest modification [19].

In contrast to this the application of the widely used crystal holders of an old type of construction does not allow the width of the line and the intensity of the line to be kept constant for a sufficiently large part of the line as a result of the imperfect bending of the crystals in them. The value of r, e.g., characterizing the width of the line in this case can change sometimes by as much as 50% for a displacement of 30-40 mm along the line. Therefore when constructing calibration curves or carrying out analysis, a definite part of the line chosen once and for all should be used all the time. With this aim in view, measurements of the width of the line should always be carried out at the point along its length where its maximum intensity is observed.

When such a method of measurement is adopted then the accuracy is not affected even by the notorious effect of "spectrum creep", which is known to be connected with an insufficient stability of the position of the focal point of the X-ray tube of the spectrograph and usually causes the X-ray spectroscopist a lot of trouble. The possible error in choosing the position of the point at which the width is measured does not in this case exceed 1 mm, while the error in measuring the width of the line which is related to the error of choosing the position of the point is considerably lower than the statistical error of the measurement.

As the practical use of this new analytical method of getting stable results showed, it is essential to take into account yet another possible source of error in measuring the width of the spectral lines. The width of the lines, just like the relative intensity for different wave lengths[1], depends on the angle of rotation of the anticathode surface of the spectrograph tube in relation to the horizontal surface - α For this reason the size of this angle would be definitely fixed when carrying out an analysis. According to our experimental results, the optimum value of α should be near to 25°.

The quantitative X-ray spectrographic methods of analysis considered were used for developing special analytical methods suitable for the quantitative determination of heavy elements.

The samples analyzed contained groups of elements to be determined simultaneously in amounts from 1 - 15%, the relative content in the samples varying from 1 : 10 and vice versa. Despite such wide variations in the contents of the elements in the samples, corresponding to variations in the blackening of the lines of 7 - 10 times [2], the percentage content of the standard element in them can be left unchanged. The amount of the standard element in the test is usually chosen so that the blackening of the $K_{\alpha 2}$ line of the standard element during the exposure time necessary for performing an analysis, lies within the range of S = 0.3 to S = 0.7. Under these conditions, as special experiments showed, the analytical results obtained by both methods are in good agreement with each other; their mean

---

1) This phenomenon is explained fundamentally by the difference in the values of the absorption for the two lines in the surface layer of the anode on which the test sample is placed.

2) It is well known that in the analytical methods used hitherto, blackening of the lines should not differ by more than 2 - 2.5 times in order to avoid large errors.

accuracy is not less than 6 - 10% of the actual content of each of the elements which are being determined simultaneously. For some concentrations and for favorable ratios of the amounts of the standard elements in the test mixtures the accuracy of their determination by the method described increases. This increase in accuracy is connected with the fact that the magnitude of the error in measurement calculated e.g., for the first of the methods considered, according to the formula

$$\Delta = \frac{2\left(\frac{\Gamma}{x}\right)^2 \frac{dx}{x}}{\left[1+\left(\frac{\Gamma}{x}\right)^2\right]^2}, \qquad (3)$$

changes regularly with the ratio of the intensities compared, I/I_0, and attains a maximum value in the region where this ratio has its mean values. From equation (3) it also follows incidentally that for $\Gamma/x = \text{const}$ the error in measurement is less, the greater x, i.e., the wider the profile of the standard line used by the investigator.

This conclusion is in good agreement with experimental observations.

Methods of Analysis Based on the use of the Transformed Characteristic Curve of the Emulsion

The P-Transformation and its Properties. In the previous paragraph consideration was given to one of the methods whereby during X-Ray spectrographic analysis, it is possible to overcome difficulties connected with the non-linear characteristic curve of the emulsion of the photographic material used. The second approach capable of leading to an improvement in the methods of X-Ray spectrographic analysis is an examination of the possibilities of "rectifying" the characteristic curve used for analysis.

Despite the fact that both these approaches to the problem are directed to the same end, have many points in common, and by the correct use of the results obtained from each method are capable of essentially supplementing each other, each approach has its own independent significance and requires special consideration. This is more expedient, in contrast to that which was true in considering the first group of analytical methods; in the last case the X-ray spectroscopist has the possibility of relying on the experience and some actual results obtained by workers in optics [20, 21, 22] who have for a long time been using (in addition to) the blackening $S = \log i_0/i$, the value of $W = \log(i_0/i - 1)$ which in a number of cases enables (in the coordinates $W - \log I$) the "latitude of the emulsion" of the photographic material to be increased at the expense of the underexposure region. Here as usual i_0 and i are the values of the galvanometer kicks, which correspond to the places on the photographic plate not subjected to the action of light, and the blackened places respectively.

In general it is natural to pose the question of looking for, and using a sufficiently simple transformation for carrying out X-Ray spectrographic investigations whereby a well defined comparison can be made of such values of some function P, as would lie fairly accurately on the straight line (4) with the values of S for a wide blackening range (e.g., from $S = 0.1$ to $S = 2$).

$$P = \gamma_P \log I - i_p \qquad (4)$$

where γ_P and i_P are constants, while I is the intensity of the monochromatic X-Ray radiation registered by means of a photographic film. Bearing in mind that in virtue of what was said above the function P for certain special values of the coefficients determining its form, should agree with W and that the curve relating W to $\log I$ in the underexposure region (in which differences in the values of W and S become important) bends towards the side opposite to the characteristic curve

$\underline{S} = \underline{S}(\log I)$, it is natural to propose that in the first approximation the function which answers condition (4) can be represented in the form $\underline{P} = \underline{W} + \underline{1}(\underline{S} - \underline{W})$, where $\underline{1}$ is a constant which is characteristic of the chosen type of emulsion.

In order to construct and use the P-transformation in practice it is necessary to have some information on two of its characteristic functions $\underline{1}$ and γ_P. Information on the third constant i_p is not essential for the solution of the majority of analytical problems. The coefficient $\underline{1}$ can be determined by several methods. The first of these methods, which is completely analogous to the method used in optics [22], assumes a knowledge of the characteristic curve of the emulsion $-S = \underline{S}(I)$ for the type of photographic materials used. According to this method two intervals differing in size $\Delta \log I$ are chosen on the abscissa of the blackening curve; one in the underexposed region, the other on the straight line part of the curve. Within the limits of each of the intervals chosen, the values of the increase in blackening ΔS and the values of ΔW corresponding to them are determined. Further using the fact that according to (4) $\Delta P_1 = \Delta P_2$ the value of $\underline{1}$ is calculated by the formula

$$\underline{1} = \frac{\Delta W_2 - \Delta W_1}{\Delta S_1 - \Delta S_2 + (\Delta W_2 - \Delta W_1)} \qquad (5)$$

It is more convenient to use the second method in those cases where the blackening curve is not known. In this case in order to calculate the required constant of the $\underline{P}$ transformation it is possible to use the fact that the ratio of the intensities of the $K\alpha_{1,2}$ doublet components of the elements is constant. A constant interval, approximately 0.3, corresponds to this ratio on the abscissa of the characteristic curve of the emulsion. Therefore, the $K\alpha_{1,2}$ lines of an element are registered on the test film twice so that the blackening of each of the lines in the doublet in one case exceeds $S = 0.8$ (the limit of the normal blackening region for X-Rays) and in the other case is less. Having made the corresponding measurements it is not difficult then to calculate the value of the requisite parameter of the transformation by means of a formula analogous to (5). Simultaneously on the basis of the results of the same group of measurements the coefficient of contrast of the emulsion can also be determined, γ_S.

Similarily for the determination of $\underline{1}$ a method can be used which is based on the artificial weakening of one of the spectral lines by means of an absorber of known density. This method, however, in the majority of cases is not so convenient as that described above.

If the blackening curve is known then a knowledge of the transformation parameter $\underline{1}$ enables the curve $P = P(\log I)$ to be drawn and the second of the quantities γ_P of interest to the analyst to be determined experimentally. If the characteristic curve is not known then the value of γ_P can be calculated by means of the relation

$$\gamma_P = \gamma_S \left[\underline{1} + (1 - \underline{1}) \frac{d\overline{W}}{dS} \right] \qquad (6)$$

where $d\overline{W}/dS = 10^{\overline{S - W}}$ is the mean value of the product dW/dS within the limits of the straight line part of the blackening curve. It is possible to show that for the films normally used in X-Ray spectrography dW/dS should be very nearly 1.08.

We shall now consider the results of an experimental study of the properties of the P-transformation in the X-Ray part of the spectrum.

Several types of film were studied including: aerofilm, negative type "A" film, positive type "nitro 1" film, and the X-Ray films "XX", and "Agfa". The effect of various developers was studied in which the degree of contrast and the capacity of giving fine grain development differed. The purpose of these experiments was to verify the correctness of the fundamental relations appertaining to

the transformation considered in the X-Ray part of the spectrum, and a study of the relation between the parameters of this transformation and the wave length of the rays registered on the film. It is only after doing this that it is expedient to consider some general questions of procedure connected with the use of the W-transformation in investigating X-Ray emission spectra.

In all the experiments described a blackening curve was constructed by the application of a method [14] which is based on using the law of change in intensity along the contour of the X-Ray spectral lines.

A group of curves which is typical of our experiments is shown in Figs. 1 and 2. The curves in Fig. 1 represent respectively the blackening curve, and its corresponding curve relating the function P and log I obtained with an X-Ray film of the "XX" type using a normal developer in a wave length region of ca. 1400 XU. Fig. 2 shows the same curve for a shorter wave length part of the spectrum (λ = 700 - 800 XU). An example of the method of calculating the transformed characteristic curve is represented in Table 1.

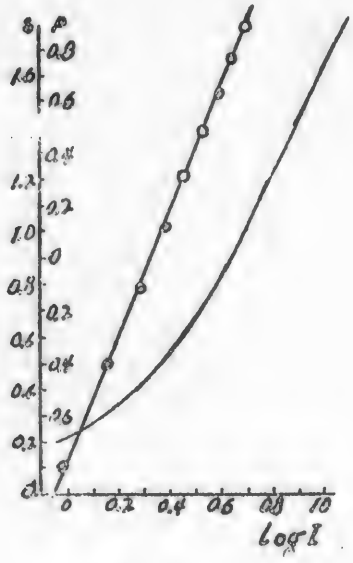


Fig. 1

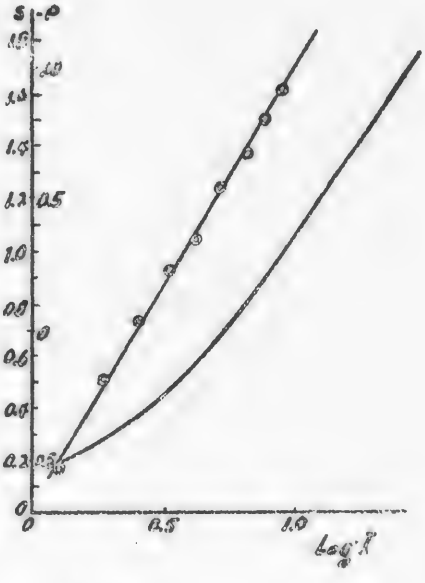


Fig. 2

TABLE 1

S	W	S − W	−0,65 (S − W)	P
0.1	−0.587	+0.687	−0.446	−1.033
0.2	−0.233	0.433	−0.282	−0.515
0.3	−0.002	0.302	−0.196	−0.198
0.4	+0.180	0.220	−0.143	+0.037
0.5	+0.335	0.165	−0.107	+0.228
0.6	+0.474	0.126	−0.082	+0.392
0.7	+0.603	0.097	−0.063	+0.540
0.8	+0.725	0.075	−0.049	+0.676
0.9	+0.842	0.058	−0.038	+0.804
1.0	+0.952	0.046	−0.030	+0.922

It is evident that in both cases the characteristic curve of the emulsion can be equally well "rectified" in the region for S = 0.1 to blackening values which

are equal to or even exceed S = 2 by means of the P-transformation. In the part of the spectrum considered there is a regular change in both the coefficient of contrast of the film and in the absolute value of the coeffieient $\underline{1}$ which has a negative sign, with decreasing wave length of the X-Rays. In this part therefore the values of the second constant which are near in magnitude usually correspond to near values of the first of these constants. Thus the relation between these values can be represented by the smooth curve depicted in Fig. 3. Here, the values of the coefficient of contrast of the film are plotted along the abscissa while the corresponding mean values of $\underline{1}$[1)] are plotted along the ordinate.

The relation between the coefficient of contrast and the wave length in the part of the spectrum considered is represented graphically in Fig. 4. It is noteworthy that alongside the almost complete constancy of this value in one region of the spectrum, in another part a regular change is observed which is sufficient to introduce appreciable distortions into the results of quantitative X-Ray spectrographic analysis in those cases where it is not specially taken into account by the analyst.

In parallel with these experiments the changes in value of γ_S with the type of photographic material used were studied. As the experiments carried out under completely identical developing conditions showed, the changes within the limit of the film of a definite type are insignificant. At the same time on switching from one type of film to another the value of γ_S changes appreciably.

Thus, for the films which we studied, the value of the maximum coefficient of contrast for X-Rays for a wave length of ca 1500 XU was a minumum (γ_S = 1.5) for negative highly sensitive emulsions. For the special types of emulsion used in aerial photography and also the X-Ray films of type "Agfa" and "positive nitro-1" the value of γ_S remained practically constant at 2.5. Films of the "XX" type were characterized by an intermediate value of γ_S = 2. It was shown in a series of comparative tests that for films of different classes (e.g. "XX" and "Agfa") a similar type of relation exists between the values of the coefficient of contrast and wave length. The curves obtained were completely identical and were only displaced relative to each other from the ordinate.

Special consideration was given to verification of the validity of relation (6). The results obtained are adduced in Table 2. Here k_E and k_T are the experimental and theoretical values of the coefficient of proportionality between γ_S and γ_P.

$$\eta = \frac{k_E}{k_T}$$

TABLE 2

Element	λ	γ_S	γ_P	$\underline{1}$	k_E	k_T	η
Cu	1537	2.06	2.50	-1.30	1.21	1.16	1.04
Zn	1432	1.96	2.36	-1.20	1.21	1.18	1.03
Ga	1337	1.80	2.06	-0.75	1.14	1.14	1.00
As	1177	1.60	1.90	-0.67	1.12	1.11	1.01
Y,Zr,Nb and Mo	870-700	1.45	1.67	-0.65	1.15	1.13	1.02

1) The value of $\underline{1}$ depends to a fairly large extent on the path of the blackening curve in the region of underexposure, where errors in the determination of the position of separate points of the characteristic curve increase for a variety of reasons. Therefore in order to calculate the coefficient in which we are interested it is expedient to take the mean of the results of a large number of parallel sensitometric experiments as a preliminary.

From a consideration of this table it can be stated that if the analyst does not have a blackening curve at his disposal, then relation (6) in which dW/dS can be assumed to be equal to 1.08 is completely suitable for calculating the value of .

The accuracy with with which this parameter of the P-transformation can be calculated is not less than the accuracy of the sensitometric test itself.

In a special series of experiments a study was made of the effect of the conditions under which the X-Ray spectrograms were developed on the form of the transformation function. Experiments were made using the copper $K\alpha_{1,2}$ doublet. The spectral lines were registered on "Agfa" films. The time of development and the composition of the developer were both varied. Three types of developer were used (I) contrast; (II) normal, and (III) fine grain.

An examination of the experimental results obtained leads to the conclusion that the maximum coefficient of contrast which can be obtained by means of a selected type of emulsion changes very little with the composition of the developer. For the three types of developer mentioned above the respective values of the maximum coefficient of contrast were 3.2;3; and 2.9. One of the curves relating γS to the development time obtained with a normal developer is shown in Fig. 5. The developers are distinguished only by the rate of development and the intensity of the fog developed on the spectrogram. On the other hand a change in the composition of the developer or in the developing conditions which often lead to an appreciable change in the form of the characteristic curve of the emulsion in the region of underexposure, or to a displacement of the limits of its straight line part, appreciably affect the value and even the sign of the basic parameter of the P-transformation, viz., the coefficient l. When this happens, however, no direct connection can be observed between the composition of the developer, the rate with which it acts or the degree of "contrast", and the change in value of the transformation parameter. Thus in our experiments there is practically no difference in the value of this constant for the developers I and III, which differ most from each other in their properties. On the other hand the value of this constant for I and III differs essentially from the value of the constant characterizing the P-transformation when using Developer II. The value of γ_P as was to be expected changes with changes in l so that in each case it can be calculated by relation (6).

2. Use of the P-Transformation for X-Ray Spectrographic analysis. The use of the P-transformation enables many of the questions which the analyst is constantly coming up against in carrying out quantitative X-Ray spectral analysis to be solved more simply and with greater precision than has been possible hitherto. Despite the limited framework of the present article we shall consider some of these questions in particular.

a) The Calculation of the Continuous Background of X-Ray Spectrograms and its Application as an Internal Standard for Quantitative X-Ray Spectrographic Analysis. The characteristic lines of the X-Ray spectra which are used for carrying out quantitative spectral analysis are always located on a more or less intense continuous background. Calculation and elimination of the background present an important and not always easily soluble problem. Various investigators often use for this purpose different and not always sufficiently precise methods. In those cases where the background of the X-Ray spectrograms appears uniform, it is sometimes completely ignored by analysts who depart from the view that as a consequence of the curvelinearity of the characteristic curve of the emulsion, the effect of a background of the same value on the blackening of lines of different intensities must be different.

The P-transformation, by means of which it has already been shown the characteristic curves used for analysis can be "rectified", enables this problem to be

solved easily and accurately[1]. Let the value $\underline{1}$, determining the form of the P-transformation, be known for a given type of emulsion and for given developing conditions. Then a knowledge of this constant enables the mutual relation between the blackening $\underline{S}$ of the film and the value of the function $\underline{P}$, satisfying condition (4) to be found. Experimentally only the change in blackening of the line at its maximum S_{L+B} and the blackening of the background S_B of the spectrogram at a definite distance from the line are measured.

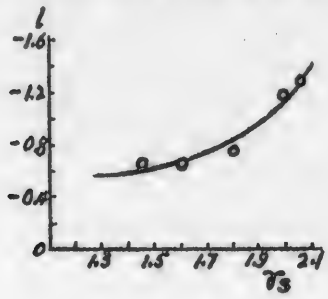


Fig. 3

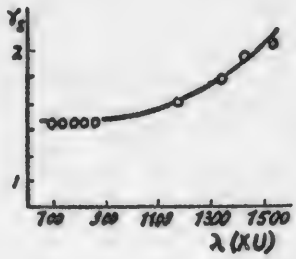


Fig. 4

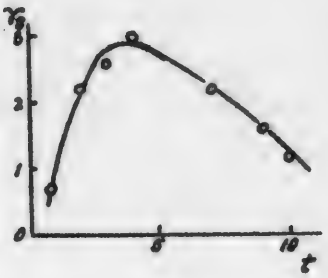


Fig. 5

Calculating the background of the spectrogram means finding the blackening S_L on the basis of a knowledge of the quantities measured experimentally, S_L being the blackening of the line if there were no background at all. A P-transformation is realized. In order to do this the values of P_{L+B} and P_B corresponding to the blackenings S_{L+B} and S_B respectively are calculated.

In accordance with the postulated problem we shall look for P_L in the form

$$P_L = P_{L+B} - \gamma_P D, \tag{7}$$

where D is a correction appertaining to the determination.

Having substituted in formula (7) the values of P from formula (4) and carrying out the necessary simplifications we get

$$D = \log I_{L+B} - \log I_L \tag{8}$$

which is equivalent to the equation

$$D = \log \frac{I_{L+B}}{I_B} - \log \frac{I_L}{I_B} . \tag{9}$$

Assuming that $I_{L+B} = I_L + I_B$ and putting $I_{L+B}/I_B = k$, it is possible to transform (9) into its final form

$$D = \log k - \log (k - 1), \tag{10}$$

in which according to formula (4)

$$\log k = \frac{P_{L+B} - P_B}{\gamma_P} \tag{11}$$

---

[1] This was considered in optical spectroscopy in 1942 [21].

It is particularly convenient to use the relation between D and k if it is represented in the form given in the table (vide e.g. [23]).

Thus a knowledge of P_{L+B}, P_B and γ_P enables one to calculate precisely the effect of the continuous background, to calculate the value of P_L according to (7), and if necessary to find the blackening S_L corresponding to this value of the P-function. In this connection therefore the difficulties which crop up during attempts to use the background of X-Ray spectrograms as an internal standard for carrying out quantitative X-Ray spectrographic analysis[1] are easily surmountable.

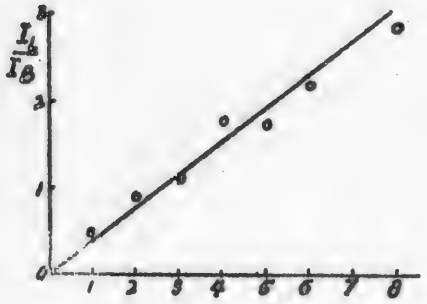


Fig. 6

The application of the P-transformation enables us by the use of the values of P_{L+B} and P_B determined experimentally, to calculate directly the value of the ratio of the intensities of the line and background which is of interest to the analyst using the fact that

$$\frac{I_L}{I_B} = \frac{I_{L+B} - I_B}{I_B} = k - 1,$$

where k is the root of equation (11).

As our experiments have shown (vide e.g., Fig. 6) this method, which is distinguished by its simplicity and by a number of other advantages, can be successfully used immediately for semi-quantitative determination of elements in objects of a complex composition with the normal order of accuracy for such determinations, ca. 20% of the actual value.

There is no doubt that after the introduction into X-ray spectrographic laboratory practice of new high voltage equipment, whereby the operating conditions of the X-Ray tube of the spectrograph can be maintained at a high level of stability, this method will enable analyses to be carried out with much greater accuracy. This is connected with the fact that the different degree of the relation between intensity of the line and background and the voltage makes the accuracy of the method described dependent to a greater extent than that of other methods, on the stability of the high tension applied to the X-Ray tube.

b) A Quantitative X-Ray Spectrographic Method of Analysis. The use of the P-transformation enables one to simplify and essentially improve the X-Ray spectrographic method of analysis. By means of it one simple, uniform, scheme of analysis, the limits of which are sufficiently wide, can be planned instead of the many special analytical methods in use at present. Let us consider the question in its most general form. Let the values of P_L' and P_L'' be known, they correspond to the two lines compared by the analysis carried out. The wave lengths of these two lines differ essentially from each other[3] In general, this means that the coefficients of the P-transformation γ_P and i_P for the lines with the wave lengths considered are different, therefore

$$P_L' = \gamma_P \log I_L' - i_P' \quad \text{while} \quad P_L'' = \gamma_P'' \log I_L'' - i_P'' .$$

If we consider the difference $P_L' - P_L''$. It will obviously be equal to

---

1) This method which was proposed as long ago as 1942 [24] is at present winning its rightful place in optical spectroscopy.

2) Both P_L' and P_L'' are reduced to a null background by means of the method, described in the previous paragraph.

$$P'_L - P''_L = \gamma'_P \log I'_L - \gamma''_P \log I''_L + i''_P - i'_P$$

Let $\gamma''_P = \gamma_P \pm \delta$,then

$$P'_L - P''_L = \gamma'_P \log \frac{I'_L}{I''_L} \pm \delta \log I''_L + (i''_P - i'_P),$$

from which

$$\frac{P'_L - P''_L}{\gamma'_P} = \log \frac{I'_L}{I''_L} + \frac{i''_P - i'_P \pm \delta \log I''_L}{\gamma'_P} .$$

Assuming as usual that $\underline{I} = \underline{kc}$, where $\underline{c}$ is the atomic percentage of the element in the test, we get the equation

$$\frac{P'_L - P''_L}{\gamma'_P} = \log \frac{c'}{c''} + \left[\frac{i''_P - i'_P}{\gamma'_P} + \log \frac{k'}{k''} \pm \frac{\delta}{\gamma'_P} \log I''_L \right], \qquad (12)$$

where since $\delta \gg \gamma_P$, the expression in brackets can, to a first approximation be considered as a constant which is characteristic of the pair of lines chosen, and of a given type of emulsion.

Equation (12) written in the form

$$\frac{P'_L - P''_L}{\gamma'_P} = \log \frac{c'}{c''} + a, \qquad (13)$$

should be verified in a wide content range of the test element. Experimental tests confirm the correctness of this conclusion. One of the curves obtained during these tests is given in Fig. 7. The constant can be determined from the condition that for $P'_L = P''_L$, $a = \log \frac{c''}{c'}$. In some special cases however it is practically zero. This naturally simplifies the development and carrying out of the analysis.

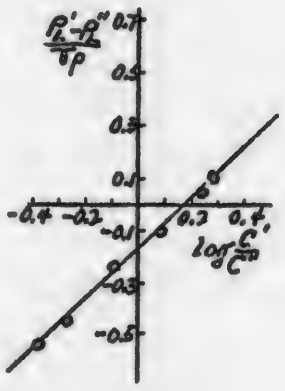


Fig. 7

SUMMARY

1. Results are given of a comparative study of two new methods of X-Ray spectrographic analysis which are based on the use of the form of the spectral lines. It has been shown that if a number of conditions are observed both the analytical methods considered lead to results which are in good agreement. The mean accuracy of the analysis is 6 - 10% of the actual content of an element and increases in certain concentration ranges.

2. The possibility of "rectifying" the characteristic curve of the photographic emulsion by means of the P-transformation has been demonstrated, and the properties of this transformation have been studied in the X-Ray part of the spectrum. A relation between the basic parameters of this transformation and the wave length of the light and the developing conditions respectively has been demonstrated.

Possible ways of using this P-transformation for carrying out quantitative X-Ray spectrographic analysis have been indicated.

Received August 4, 1952

LITERATURE CITED

[1] I.Borovsky and M.Blokhin, "X-Ray Spectrographic Analysis." United Sci. Tech. Press 1939.

[2] G.Hevesy, Alexander, Wurstlin, Chem. Z. 181, 95 (1929); 164, 316 (1927).

[3] G.Hevesy, Bohm, Chem. Z. 164 69 (1927).

[4] I.Borovsky and M.Blokhin, Bull. Acad. Sci. Sect. Geol. No. 1 and 5, 929 (1937).

[5] I.Borovsky, M.Blokhin, and L.Grzhibovskaya, Bull. Acad. Sci. Ser. Phys. No.1, 112 (1940).

[6] T.Sahama, K.Rankama, V.Heinasko, Bull. Commis. geol. Finlande,N.128, 21 (1943).

[7] V.Protopov, Factory Labs. 14, 52 (1948).

[8] E.Vainshtein and N.Turanskaya, J. Anal. Chem. 4, 323 (1949).

[9] E.Vainshtein, "The X-Ray spectra of atoms in molecules of chemical compounds and in alloys." USSR Acad. Sci. Press, 1950.

[10] V.Gerlakh and V.Rolvagen, Metalwirts, 16, 1083 (1937).

[11] P.Coneur, Met. Soc. Roy. Sciences,Liege 5, 1 (1942).

[12] P.Coneur, J. of the optical Soc. Am.36, 948 (1946).

[13] I.Borovsky, Factory Labs. 11, 1935 (1948).

[14] E.Vainshtein and N.Turnaskaya, J. Anal. Chem. 7, 180 (1952).

[15] E.Vainshtein, K.Narbutt and A.Gilvarg, Proc. Insti. Crystal. 6, 207 (1951).

[16] W.Wooster, G.Ramanchandran, A.Lang, J. of Scien. Inst. 26, 156 (1949).

[17] I.Borovsky, Proc.Acad.Sci.USSR, 72, 485 (1950).

[18] A.Gilvarg,Proc.Acad.Sci.USSR, 72, 489 (1950).

[19] A.Pivovarov and E.Vainshtein, J. Anal. Chem. 6, 386 (1951).

[20] A.Sampson and Backer, Proc. Roy. Soc., Edinburgh,45,166 (1925).

[21] M.Honerjager, Sohm and H.Kaiser, Spectrochemica Acta,2, 396 (1942).

[22] H.Kaiser, Spectrochemica Acta 3, 159 (1948).

[23] V.Prokofiev, "Photographic methods of quantitative spectral analysis of metals and alloys." Part II,State Institute of Technology,1951.

[24] S.Borovik,Proc.Acad.Sci.USSR, 36, 186 (1942).

THE APPLICATION OF THE ION-EXCHANGE CHROMATOGRAPHIC METHOD IN THE ANALYSIS OF COPPER-IRON CERAMIC ALLOYS AND BRONZES

D.I.Ryabchikov and V.E.Bukhtiarov

Tsvet's chromatographic method [1] in all its forms: adsorption, precipitation, distribution, and ion-exchange chromatography, has found more and wider applications in analytical chemistry in recent years.

Ion-exchange chromatography has been applied sucessfully for the analysis of cations. This method cannot be regarded as an independent method in analytical chemistry, but it represents an exceedingly important intermediate stage in the analysis of complex materials.

By means of ion-exchange it is possible to separate the components of a mixture in a pure state and subsequently to determine the nature and amount of each of them by normal chemical or physico-chemical methods.

Ion-exchage chromatography can be applied in chemical analysis, e.g., for concentrating salts which are found in dilute natural mineral solution or in industrial wastes before subsequent determination of their total concentration or the concentration of individual components of the mixutre. Of vital importance in analytical procedure is the removal of ions which interfere with the determination of certain elements. This removal can be effected by the use of ion-exchange columns e.g. the separation of iron and aluminum ions from any sulfuric or phosphoric acids present in solution. A prospect with the greatest possibilities for analytical chemistry is the separation of certain cations from mixtures of them by transforming them into anionic forms on the basis of their amphoteric character or by complex formation. It is also possible to separate elements of similar properties by using "cationite" (cation-exchange resins) columns in conjunction with complex compounds of the components of the mixture being analyzed which are of different stabilities. Further enumeration will not exhaust the possible applications of ion-exchange chromatography in chemical analysis.

Natural ion-exchange compounds, both organic (substances rich in humic acids - peat, brown coal,) and inorganic (aluminosilicates) have been widely used in practice for a comparatively long time. But the application of ion-exchange resins increased considerably after the production of synthetic inorganic ion-exchange materials (permutites) and particularly after the preparation of synthetic organic resins capable of exchange-ionites.

All the synthetic exchange resins known at the present can be divided into two groups. To the first group belong those resins with acid properties and which are capable of exchanging cations-cationites. They are polymerization or condensation products of phenol or styrene, and their derivatives with formaldehyde. As a result of special treatment the active acid groups $-SO_3H$; $-CH_2SO_3H$; $-COOH$; phenol groups $-OH$ etc., enter into their composition. Because the active groups are structurally linked with the resin skeleton they cannot go into solution. Only the hydrogen ions of these groups ($R-SO_3H$) or cations which have substituted hydrogen remain mobile.

The second group is comprised of resins possessing basic properties and capable of exchanging anions-anionites. The ion-exchange properties of these anionites are determined by the presence of amine or imine groups in them.

The exchange and regeneration processes of ion-exchange resins can be described by the equations for the following reactions

Cationites $nRH + Me^{n+} = R_nMe + nH^+$ (exchange)

$R_nMe + nH^+ = nRH + Me^{n+}$ (regeneration)

where Me = Na^+, K^+, Mg^{2+}, Al^{3+}, Fe^{3+}, etc.

Anionites $nROH + An^{n-} = R_nAn + nOn^-$ (exchange)

$R_nAn + nOH^- = nROH + An^{n-}$ (regeneration)

where An = Cl^-, SO_4^{2-}, PO_4^{3-} etc..

The ion-exchange process can be considered as a heterogenous process between the active groups of the resin and the ions in solution, The reaction proceeds in accordance with the law of mass action.

Synthetic resins which are to be used as ion-exchange compounds must satisfy a number of requirements. Primarily they must be stable in different chemical media and possess high mechanical stability in the dry state and also particularly in the swollen state. The resins used for analytical purposes, while possessing a good absorptive capacity, should at the same time under the respective conditions give up the absorbed ions completely. These requirements are satisfied to a large extent by makes of resins where they are prepared in the form of small spheroids. Ionites prepared by breaking down hard masses of resin often have uneven grain surface and therefore as a rule they hold a part of the ions absorbed by them very firmly.

The comparative characteristics of some ion-exchange resins both of Russian and foreign manufacture were studied by Ryabchikov, Senyavin, and Filippova [2]. Of the Russian makes the most suitable for analysis are the cationites SBS, SDV-1 and SD-2 and the anionite MMG-1.

A large amount of work has been devoted to the application of ion-exchange resins in analytical chemistry. A detailed literature survey was given in the article of Ryabchikov and Teretev [3]. Several investigations have been made by Soviet analysts [4-6] on the separation of mixtures of metals in the course of their analytical determination.

In the present article some examples of the use of exchange-ion resins for the separation of individual metals in the analysis of alloys are considered.

Separation of Copper From Iron in the Analysis of Copper-Iron Ceramic Alloys

The normal method of separating copper and iron is based on the differences in their behavior with ammonia, but as a consequence of the adsorption of copper by the ferric hydroxide precipitate, precipitation has to be repeated several times. Even then the desired result is not always attained, and the analysis takes a long time. The application of cation-exchange columns radically improves the process of separating these metals

The fundamental idea of the chromatographic method consists in passing a solution through a layer of cationite in one definite direction; this is achieved by means of the simple apparatus shown in the diagram.[1] This method of normal filtration through a column of cationite is called frontal analysis. This method was used throughout the investigation.

[1] See Plate, page 431.

The column was filled with the cationite SBS[1] in the hydrogen form.

The separation of copper and iron is possible if one of these elements, e.g., iron can be converted into a complex anion; in such a case, the copper in the form of its simple ion will be held by the cationite in the column as a result of the reaction:

$$2R\text{-}SO_3H + Cu^{2+} = (R\text{-}SO_3)_2Cu + 2H^+ ,$$

while iron, being in the form of an anion, will pass through into the filtrate.

Sodium pyrophosphate was chosen as the complexing agent. However it was shown that the sodium pyrophosphate, for nearly neutral solutions, reacts with both metals forming complex compounds according to the equations:

$$2Fe_2(SO_4)_3 + 6Na_4P_2O_7 = 2Na_6[Fe_2(P_2O_7)_3] + 6Na_2SO_4 ,$$

$$CuSO_4 + Na_4P_2O_7 = Na_2[CuP_2O_7] + Na_2SO_4 .$$

In practice at a pH of 7.5, as a result of complex formation between both the copper and iron salts and sodium pyrophosphate, both metals passed through into the filtrate on passing a solution of the mixture through a cationite column.

The situation can be basically altered if the pH of the original solution is adjusted to pH 10-11 (by addition of ammonia). In this case the pyrophosphate complex of iron remains unchanged because of its high stability. The pyrophosphate complex of copper, being less stable, changes in ammoniacal media according to the reaction:

$$Na_2[CuP_2O_7] + 4NH_4OH + Na_2SO_4 = [Cu(NH_3)_4]SO_4 + Na_4P_2O_7 + 4H_2O .$$

The copper becomes a part of the cation in the complex formed.

Thus by the successive treatment of the solution, being analyzed with pyrophosphate and ammonia, the two metals become parts of different ions; iron becomes part of the anion $[Fe_2(P_2O_7)_3]^{6-}$, while copper becomes part of the cation $[Cu(NH_3)_4]^{2+}$.

On passing the test solution through a column of cationite, the iron passes through into the filtrate while the copper is retained on the column combined with the active group of the resin. The separation of copper and iron and their subsequent determination were carried out as follows;

1 g of alloy was dissolved in 30 ml 30% HNO_3 and 20 ml 10% H_2SO_4 with heating until white fumes of sulfuric acid appeared. The salts obtained were dissolved and the solution made up to 250 ml in a standard flask. For each determination 50 ml of solution was taken; to this aliquot was added a saturated solution of sodium pyrophosphate until the simple pyrophosphates originally formed dissolved again. To the solution of complex pyrophosphates thus obtained was added 25 ml of concentrated ammonia and after careful mixing the solution was filtered through a cationite column in which the resin was in the hydrogen form, at the rate of 4 ml/minute. The residue in the beaker and the iron from the column were washed with 3% ammonia solution. 10% KCNS was used to test that all the iron had been removed from the column. 50 ml of 20% NaOH was added to the filtrate containing iron and the solution heated until it clarified. The precipitate of ferric hydroxide formed was then filtered and dissolved in 20% hot hydrochloric acid; the solution was transferred to a 250 ml standard flask and made up to volume. The iron was then determined in an aliquot by means of permanganate.

---

[1] This cation was prepared at the Plastics Division of the D.I.Mendeleev Chemico-Technological Institute, Moscow

The copper was stripped from the column by eluting with 20% HCl to start with, and then with 10% HCl. That all the copper had been removed was checked by the absence of a blue color when 5 drops of the eluent from the column was added to a solution of potassium iodide and starch. 15 ml of concentrated H_2SO_4 was added to the filtrate containing copper, after which the filtrate was evaporated till white fumes of sulfuric acid appeared. The salts obtained were dissolved in 100 ml of water and the copper determined iodometrically.

Results for the determination of copper and iron in copper-iron ceramic alloys using SBS are given in Table 1.

These results show that satisfactory agreement with those obtained by another method.

Tartrates and citrates were also tested as potential complexing agents. However these salts formed such stable complexes with iron that the metal could not be removed completely from the filtrate even with concentrated alkalis.

TABLE 1

No. of Expt.	Normal Method (in %)		By the use of cationite (in %)	
	Copper	Iron	Copper	Iron
1	59.64; 59.58; 59.56	39.60; 39.60; 40.01	59.56; 59.80; 59.64; 59 46; 59.56	39.74; 39.72; 39.74; 39.45; 39.45
2	49.78; 49 48; 49.72	49.82; 49,54; 49.66	49.76; 49 74; 49.80; 49 76; 49.80	49.54; 49.54; 49.53; 49.52; 49.52
3	29.82; 29 96; 30.00	68.54; 68,39; 68.72	29.84; 29 96; 30.00; 29 96	68.54; 68.71; 68.55; 68.54;

In parallel with the cationite SBS we used the American product "Dowex 50". Although Dowex 50 has a greater absorptive capacity than SBS, we did not get such good results with it.

Separation of Copper From Aluminum in the Analysis of Bronzes

Bronzes of marks BrA5, BrA7 and BrA10 have copper as the basic component with additions of from 4-11% aluminum.

The normal analytical method for these bronzes is based on either electrolytic separation of copper or its precipitation with thiosulfate and subsequent iodometric determination, while the aluminum is determined in the filtrate by means of 8-hydroxyquinoline. It follows from this that for the first method (electrolytic separation) mentioned, platinum electrodes, etc., are necessary, while the second method takes a long time to perform.

Copper can be readily separated from aluminum by using a cationite column. As in the previous instance one of the elements to be separated is converted by means of a complexing agent into a complex anion (aluminum) while the other remains as the cation (copper).

Tartaric acid in ammonia solution was chosen as the complexing agent. In the presence of these reagents, aluminum forms a tartrate complex in which it forms part of the anion $[Al_2(C_4H_2O_6)_3]^{6-}$ which is formed by the reaction

$$Al_2(SO_4)_3 + 3C_4H_6O_6 + 12NH_4OH = (NH_4)_6[Al_2(C_4H_2O_6)_3] + 3(NH_4)_2SO_4 + 12H_2O \ .$$

Copper under these conditions forms part of the cation -- $[Cu(NH_3)_4]^{2+}$ which is itself formed according to the reaction

$$CuSO_4 + 4NH_4OH = [Cu(NH_3)_4]SO_4 + 4H_2O .$$

On passing a solution treated in this way through a cationite column, the aluminum passes through into the filtrate while the copper in the form of the complex cation is retained by the active groups of the resin according to the reaction:

$$2R\text{-}SO_3H + [Cu(NH_3)_4]^{2+} = (R\text{-}SO_3)_2Cu(NH_3)_4 + 2H^+ .$$

Copper and aluminum were separated by the following procedure;

0.25 g of bronze was dissolved by heating with 15 ml 30% HNO_3 and after addition of 10 ml 10% H_2SO_4 the solution was evaporated until white fumes of sulfuric acid ceased to be evolved. The salts obtained were then dissolved in 25 ml water and 2 g of tartaric acid added to the solution obtained; after this had dissolved 50 ml of concentrated ammonia was added. The solution was carefully mixed and then passed through a cationite column containing SBS in the hydrogen form. The aluminum was eluted from the column with 3% ammonia. To the filtrate obtained (ca. 400 ml) hydrochloric acid was added till a weakly acid solution was obtained, when it was evaporated to 200-250 ml. Aluminum was then precipitated from the evaporated solution, which had been made alkaline with ammonia, with 8-hydroxyquinoline. The aluminum hydroxyquinolate was finally dissolved in hydrochloric acid and the aluminum determined volumetrically by the bromate-bromide method.

The copper was removed from the cationite first with 20% and then with 10% hydrochloric acid solution. A solution of potassium iodide plus starch was used to check that all the copper had been removed. The filtrate containing the copper, after addition of 15 ml concentrated H_2SO_4, was evaporated until white fumes of sulfuric acid appeared. The salts were then dissolved in 100 ml of water and the copper determined iodometrically. Results for the determination of copper and aluminum in bronzes using SBS are given in Table 2.

TABLE 2

Type of Bronze	Normal method (in %)		By the use of cationite (in %)	
	Copper	Aluminum	Copper	Aluminum
BrA5	95.00	5.15	94.92; 94.72; 95.24	4.96; 5.12; 5.34
BrA7	92.42	7.49	92.00; 92.40; 92.40	7.58; 7.56; 7.68
BrA10	90.70	9.30	90.64; 90.52; 90.90	9.48; 9.44; 9.52

Separation of Copper, Aluminum, and Iron in the Analysis of Bronze

Bronze mark BrAFe 9-4 contains copper as the basic component, aluminum (from 8-10%) and iron (from 2-4%).

Bronze mark BrAFeMn 10-3-1.5, in addition to copper as the major component, also contains aluminum (9-11%), iron (2-4%) and manganese (1-2%). The normal chemical method of analysis is identical with that described above. After the electrolytic separation of copper, the aluminum is separated from the iron (manganese) by the usual method. The aluminum is finally determined by means of 8-hydroxyquinoline while the iron is determined by the permanganate method. Manganese is determined by the persulfate method on a separate aliquot.

The drawbacks of this method are the same as those mentioned above. The position can be radically improved if a cationite column is used for separating the

copper from aluminum and iron. As before the aluminum and iron are converted into complex anions by means of a complexing agent while the copper is absorbed by the resin as a cation.

In this rather more complicated case sodium pyrophosphate cannot be used as the complexing agent for iron, or tartaric acid for aluminum. Salicylic acid seemed to be a suitable complexing agent in this case. We established that at a pH of 10 in the presence of salicylic acid and ammonia iron and aluminum can be complexed as the anions $[Fe(Sal)_3]^{3-}$ and $[Al(Sal)_3]^{3-}$, while the copper remains in the form of the complex cation $[Cu(NH_3)_4]^{2+}$.

The [illegible] chemistry of the interaction of these metals with salicylic acid is treated in detail in the literature [7, 8].

However, because of the poor solubility of salicylic acid in water, we used sulfosalicylic acid instead. Sulfosalicylic acid is much more soluble, while it possesses complexing properties of the same order as salicylic acid.

It should be noted that if any manganese is present it will behave differently. Manganese forms a complex anion which is not stable enough so that a test solution containing manganese on passing through a column will take some of the manganese through into the filtrate with it, together with the iron and aluminum, while the rest of it is retained by the resin because of the decomposition of the complex by the active groups of the cationite.

Copper was separated from aluminum and iron and subsequently determined in production samples as follows:

0.25 g of alloy was dissolved as indicated above. The salts obtained were dissolved in 25 ml of water and 25 ml of a 20% solution of sulfosalicylic acid, and 25 ml of concentrated ammonia solution added. After the solution had been thoroughly mixed it was passed throught a cationite in its hydrogen form at the rate of 4 ml/minute. The column was eluted with 3% ammonia to remove any residues of aluminum and iron and the total volume of the filtrate made up to 400 ml. 30 ml of 20% sodium hydroxide was then added to the filtrate and heated till the solution clarified. Iron as ferric hydroxide was filtered off and determined by the permanganate method. The aluminum in solution as aluminate was acidified with hydrochloric acid. It was then precipitated from an ammoniacal solution with 8-hydroxyquinoline and determined by the bromide-bromate method. The copper was extracted from the column and determined iodometrically.

Results for the determination of copper, aluminum, and iron in the bronzes of these marks are given in Table 3.

TABLE 3

No. of sample	Normal method (in %)			By the use of cationite (in %)		
	Copper	Aluminum	Iron	Copper	Aluminum	Iron
Standard	88.05	9.80	1.97	88.00; 88.16; 88.12; 87.92	9.91; 9.72; 9.78; 9.84	1.90; 1.99; 1.99; 2.10
8	85.51	8.80	3.80	85.60; 85.30; 85.34; 85.38	8.78; 8.80; 8.80; 8.92	3.69; 3.80; 3.70; 3.76
9	81.56	10.76	7.27	81.80; 81.44; 81.60; 81.40	10.92; 10.80; 10.76; 11.00	7.20; 7.12; 6.96; 7.20
68a[1]	85.63	9.82	2.74	85.48; 85.80; 85.60; 85.64	10.08; 10.04; 10.02; 10.00	2.88; 2.64; 2.82; 2.76
2[1]	86.29	9.88	3.66	86.12; 86.48; 86.40; 86.32	9.75; 9.81; 9.86; 9.85	3.72; 3.43; 3.65; 3.67

1) There was 1.49-1.55% manganese in samples 68a and 2.

Separation of Manganese and Iron When Present Together

The chromatographic separation of this pari of metals is of interest in itself, apart from the analysis of bronzes and ceramic alloys.

Taking into account the chemical characteristics of manganese to be converted easily into the ionic state MnO_4^-, it seemed that the problem would be solved by simple oxidation of the test mixture whereby the iron would be converted into its trivalent form (Fe^{3+}). In practice however this did not work. On passing a solution containing manganese in the form of its anion through a cationite column, it was reduced as a result of the reducing properties of the resin, and in its reduced form, manganese just like iron was held back by the active groups of the resin. If the acidity was increased to any large extent, so that the manganese was retained in the septi-valent stage, then the iron also passed through into the filtrate with the manganese. It was shown that the best results were obtained when the mixture of iron and manganese was treated with a solution of ammonium oxalate at a pH of 5. Under these conditions the manganese remains as a positive bivalent ion (Mn^{2+}) while the iron becomes a part of a complex anion of the composition $[Fe(C_2O_4)_3]^{3-}$ according to the reaction:

$$FeCl_3 + 3(NH_4)_2C_2O_4 = (NH_4)_3[Fe(C_2O_4)_3] + 3NH_4Cl.$$

The oxalate complex of the iron remains stable in weakly acid solutions and is not destroyed on passing through a cationite column.

The procedure adopted was as follows:

To a neutral solution containing manganese and ferric sulfate was added 15 ml of 30% HNO_3 and 10 ml H_2SO_4, after which the solution was evaporated to white fumes of sulfuric acid. The salts obtained were dissolved in 25 ml water and 4% ammonium oxalate solution added until all the iron has been combined into a complex.

Concentrated ammonia was then added dropwise till the blue color of Congo red turned red. The solution thus prepared was passed through the column containing cationite in the hydrogen form at the rate of 4 ml/min. Any residual iron was eluted from the column with distilled water until a negative test was given with thiocyanate. The manganese was removed from the column with 10% H_2SO_4. The metals in the respective fractions were then determined by the usual methods. Results are given in Table 4.

TABLE 4

Mg taken		Mg found	
Iron	Manganese	Iron	Manganese
10.20	22.50	9.90; 10.00; 10.00	19.60; 19.90; 21.70
20.40	15.00	19.90; 19.40; 20.20	13.70; 14.60; 14.50
20.40	7.50	19.90; 19.60; 19.50	7.60; 7.00; 7.00
30.60	15.00	30.00; 29.90; 29.60	13.70; 13.20; 14.50

SUMMARY

1. Conditions have been selected [ionite (ion-exchange resin), size of column, filtration rate, complexing agents, and media] for the separation of the components of ceramic alloys and bronzes before their analysis.

2. Copper and iron can be separated by using sodium pyrophosphate in ammoniacal media as the complexing agent.

3. Copper and aluminum can be separated by using tartaric acid in ammoniacal media as the complexing agent.

4. Copper can be separated from aluminum and iron by using sulfosalicylic acid in the presence of excess ammonia as complexing agent.

5. Iron and manganese can be separated in the presence of ammonium oxalate at a pH of 5.

6. The methods developed enable copper to be determined in alloys without the use of platinum.

Received October 4, 1952

LITERATURE CITED

[1] M.S.Tsvet, "Chromatographic adsorption analysis." Acad.Sci.USSR Press,1946.

[2] D.I.Ryabchikov, M.M.Senyavin and K.V.Filippova, J. Anal. Chem. Vol.VII No. 3, 135 (1952).[1)]

[3] D.I.Ryabchikov and E.A.Terenteva, Prog. Chem. 19, 220 (1950).

[4] Yu.M.Kostrikin and Yu.Yu.Lure, Factory Labs. 14, 173 (1948).

[5] Yu.I.Usatenko and O.V.Datsenko, Factory Labs. 15, 779 (1949).

[6] Yu.Yu.Lure and N.A.Filippova, Factory Labs. 13, 539 (1947); 14, 159 (1948); 15, 771 (1949).

[7] A.K.Babko, J. Gen. Chem. XV, 745 (1945); XVII, 443 (1947); XVIII, 1607 (1948); XVI, 33 (1946).

[8] V.I.Kuznetsov, Factory Labs. 12, 278 (1946).

1) See Consultants Bureau translation, p. 153.

ALEXEI MIKHAILOVICH VASILEV

(On his 70th birthday)

This year Professor Alexei Mikhailovich Vasilev celebrates his 70th birthday and also his 45th year of scientific and teaching activity. He is one of the oldest analytical chemists of our country – a Doctor of Chemical Sciences; he has been an active worker for science and technics in the RSFSR and TASSR.

Having finished at the Perm classical preparatory school Vasilev entered the Natural Sciences, Physico-Mathematical Faculty of Kazan University in 1902. He finished his course in 1907.

In 1908 he took his state examination and got a first class diploma. Prof. F.M.Flavitsky' proposed that he stay at the University in order to prepare for a Professorship. Within one year Vasilev passed his master's degree and became a lecturer and started taking courses in "Gas Analysis". In the autumn semester of 1912 he was entrusted with the important course on "Qualitative Analysis", while from 1913 onwards he also took the course on quantitative analysis.

A.M.Vasilev's scientific and teaching activities only reached their fullest development after the Great October Socialist Revolution. In 1918 he was appointed as professor in Kazan University. He put in a great deal of work and energy in organizing an independent chair of analytical chemistry in the University, he still heads this section. He deserves credit for creating an unified course in analytical chemistry, instead of descriptive and purely empirical courses of qualitative and quantitative analysis.

In 1930 a Chemical-Technological Institute was organized in Kazan. Vasilev became a professor at the Institute and headed the chair of analytical chemistry, as he still does at present. He contributed his wide teaching experience and knowledge to the development of a new industrial college. Vasilev is a dean of the technological faculty, and serves as deputy of the director on the scientific and educational side and sometimes fills the post of Director of the Institute.

Vasilev's scientific activity is distinguished by its variety. He has published more than 100 papers mainly on inorganic and analytical chemistry. The first of his papers on analytical chemistry relate to his earlier period of scientific activity ("The application of nitron in nitric acid analysis") 1910,and "Indirect analysis of the halide salts of antimony and tin".

Vasilev has proposed quite a number of analytical methods which have been adopted in various textbooks on analytical chemistry. Of these we may note "A rapid method for the simultaneous determination of calcium and magnesium",published in 1932 in "Factory Laboratories".

This method has considerable advantages in speed and is no less accurate than other similar methods.

A.M.Vasilev also worked on volumetric gas analysis. His work on volumetric gas analysis for the determination of potassium by means of cobaltinitrite,published in 1930,is of the greatest practical significance. This method consists in the decomposition of potassium cobaltinitrite with ferrous salts to give nitric oxide.

One of the fundamental branches of his scientific activities in analytical chemistry was the study of the phenomenon of coprecipitation. Under his guidance a large amount of work was devoted to the study of the precipitation of many practically insoluble salts in the presence of various cations and anions. The precipitate of barium sulfate in the presence of trivalent iron, thorium, nitrates, chlorides, bromides, borates and the precipitates of lead sulfate, calcium oxalate and many others were studied.

It was therefore natural and not accidental that Vasilev has developed an interest in recent years in chromatography, and in particular in the study of ion exchange processes which are gaining such importance in analytical chemistry.

Vasilev's work on the washing of precipitates is worthy of attention. He proposed an original method of washing precipitates with a saturated solution of the precipitant. This method of washing was tested on various precipitates ($SrSO_4$ etc.), and took its place in several textbooks as recommended.

Of Vasilev's theoretical work in analytical chemistry his proposed formula for the extent of neutralization should be mentioned (Proc. Kazan Chem.-Tech. Inst. No. 2,1934).

This formula gives the relation between the degree of titration of a weak acid and its dissociation constant for any given hydrogen ion concentration.

This formula with the usual degree of accuracy enables one to make interesting conclusions for volumetric analysis; it is possible to determine the extent of titration of acid with various indicators; to calculate the hydrogen ion concentration in solutions of the acid salts of dibasic acids;and to calculate the amount of acid which must be neutralized in order to get a buffered solution with a given pH.

While acknowledging the importance of physico-chemical methods of analysis, he does not forget the classical methods and continues to develop them in his work. He considers the application of organic reagents in analytical chemistry of great significance and writes excellent reviews on this question which are published in the "Proc. of the Commission on Analytical chemistry".

In recent years Vasilev has turned his attention to the study of ion-exchange and the application of this technique in analysis.

His scientific activities are not confined within the walls of the University laboratories. Numerous factory laboratories in the Tatar Republic consult him on a wide range of subjects.

He plays an active part in the work of the Kazan scientific societies. He has been a member for a large number of years of the committee of the Kazan branch of the D.I.Mendeleev All-Union Chemical Society, and is one of the oldest members of the Society of Naturalists in Kazan University

With his wide knowledge and penetrating understanding of a large number of chemical problems he has written more than 50 references for scientific workers in Kazan and other cities of the Soviet Union trying for their doctor's or candidate's degree.

Vasilev's work on methods is well known. He has published a number of articles on methods of teaching analytical chemistry and has read reports on this subject at conferences. His "Collection of problems in analytical chemistry" is a valuable text book for teachers and students.

His fruitful scientific teaching and social activities have gained him acknowledgement and high rewards from the Soviet Government.

In 1940 in connection with the 10th anniversary of the Kazan Chem. Tech.

Institute and the 50th anniversary of industrial education in Kazan, the Praesidium of the Supreme Soviet of TASSR assigned to Vasilev the honorable title of Meritorious Worker in Science and Technology of the TASSR.

In 1947 he was given the same title of the RSFSR.

He was awarded the order of the Red Banner of Labor and a medal "For Valiant Service in the Patriotic war 1941-1945."

On his birthday his friends and a wide circle of Soviet Analytical chemists send him their sincerest wishes for good health, new strength and long life, and a continuation of his fruitful work for the glory and prosperity of Soviet chemistry and for the good of our beloved country.

C R I T I C I S M

A NEW AND USEFUL BOOK

N.P.Komar "A Collection of Problems, Exercises, and Questions in Qualitative Analysis". Published by Kharkov State University, Kharkov, 1952, pp. 1-230. Circulation 5000. Price 5 roubles 90 kopecks.

Despite the variety of subjects dealt with in Russian chemical literature, the publication of N.P.Komar's book fills a definite gap, because no other book has yet been devoted to qualitative analysis in which there is such a complete and penetrating exposition of the mathematical side of the chemical processes studied in qualitative analysis. Although many books have been devoted to calculations in physical chemistry and chemical thermodynamics (R.Abeg and O.Sakhur 1924; D. Noakes 1934; R.Venner 1950 etc.) and these questions are also dealt with in various textbooks on thermodynamics (A.F.Kapustinsky, 1936; J.Partington and A.V. Rakovsky, 1932; M.Kh.Karapetyants, 1949) only "Problems in Quantitative Analysis", by A.P.Musakun, A.I.Khrapovsky, S.P.Shaikind and S.M.Efrov (State Chem. Press 1950) containing the simplest calculations on quantitative determinations, and A.M.Vasilev's "Collection of problems in analytical chemistry" can be mentioned which deal with analytical chemistry. Vasilev's book is somewhat closer in content to Komar's book, but the problems in the former are simple while the system of ionic equilibrium is not considered in such detail or from so many aspects as in Komar's book.

N.G.Glinka's ("Problems and Exercises in General Chemistry", 1947), which is most like the book under review, concerns general chemistry and is designed for less advanced students.

Komar's book, which is new in concept and new by reason of its complete grasp of the whole range of questions discussed, contains fresh, new, and interesting material which has been carefully thought and worked out.

It consists of four sections.

I. Construction of equations.

II. Problems on the theory of ionic equilibria.

III. Questions and problems for oral examinations in a course on qualitative analysis.

IV. Solutions of typical problems.

The section dealing with problems in the theory of ionic equilibrium is very interesting. It deals with the calculation of the degrees of dissociation from cryoscopic data, and from electroconductivity results; calculations of equilibrium in solutions of weak acids and bases, in solutions of weak acids and their salts, and of acid salts; equilibria in systems containing two weak acids; equilibria in solutions of multibasic acids; equilibria in systems containing indicators; and equilibria in systems containing complex ions. Many problems are devoted to hydrolysis, to the calculation of the solubility product by solubility and vice versa. Calculations are made of the minimum concentrations required for the formation of precipitates; a few cases are considered of equilibrium connected with the solution of difficultly soluble compounds; equilibria connected with the solution of amphoteric hydroxides; equilibria during complex formation; equilibria in systems with oxidizing or reducing agents; and the determination of optimum concentrations of precipitant.

This list shows how wide and all embracing is the treatment given to the theory of ionic equilibrium which lies at the basis of almost all qualitative reactions in analytical chemistry.

Considerable attention is given to complex formation, beginning with the terminology, compilation of equations,and calculations of the process of complex formation. Among the tables of constants at the end of the book, Table 6 contains constants for a very large number (35) of complex ions; thus this important section is treated very thoroughly.

Oxidation – reduction processes are not treated quite so fully.

Thus problems (No. 619-638) basically reduce to dissolving metals and sulfides in acids, while very few problems of the type of No. 638,on the oxidation of the manganous ion to permanganate by lead dioxide in sulfuric acid,are given. There are however a large number of such problems in analytical chemistry,e.g.,the reduction of ferric chloride with stannous chloride, the solution of manganese dioxide in acid solutions of ferrous sulfate, etc. etc..

A table of the constants of oxidation – reduction processes is given at the end of the book (in detail on 8 pages); it would however have been more convenient to give a table of oxidation – reduction potentialswhich chemists are accustomed to use, in particular in volumetric and electrometric methods of analysis.

The main virtue of this book is its freshness and the variety of examples chosen by the author. Together with important analytical reactions and in addition to the usual elements dealt with, cesium, rubidium, and thallium often figure in the examples; problems in which methylamine crops up introduce variety into the material, since methylamine does not often turn up in such problems. True there are some defects in the consideration of elements of the 6th group; only one or two questions are devoted to selenium and tellurium, while tungsten and uranium are not included at all, although there are quite a few problems relating to these elements which could have been considered. This however does not affect the complete and all round exposition of the processes considered in this book.

The mathematical side of this book is particularly worth dwelling on. In addition to calculations which can be solved by direct substitution of the respective numerical data in the equations of physical-chemistry, the majority of the problems require considerably more complex calculation. These calculations could present a lot of difficulties to many chemists, if the solution of such problems were not adduced, and the principles used in solving them enunciated. Thanks to this the reader can pick up the methods for solving similar calculations, not only those in the book but those which crop up for similar reactions in practical analytical work.

There is no doubt that this book will be a very great help to a large number of chemists, will enable them to improve their qualifications and scientific education, and will enlarge their knowledge of chemical processes on the quantitative side. In addition it will serve as an stimulus for starting new investigations on the quantitative evaluation of processes.

The publication of this book is a valuable contribution to Soviet chemical literature.

V.V.Shcherbina

The Ultramicro Method of Chemical Analysis, p. 377.

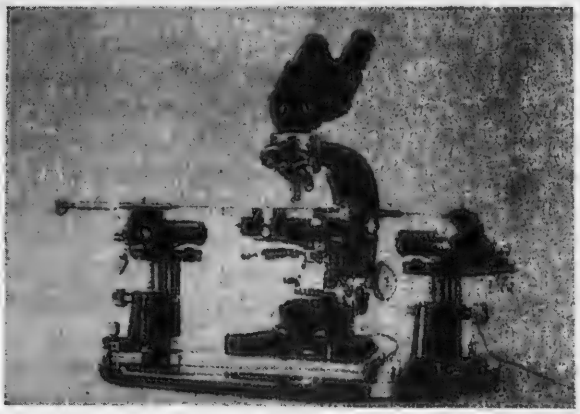


Fig. 5. Apparatus for carrying out ultramicro chemical determinations.

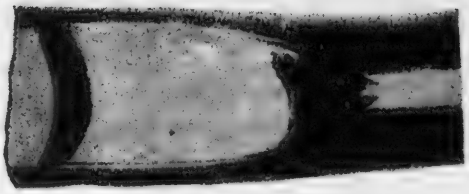


Fig. 6. Precipitate of silicic acid in an evaporated solution

Spectrophotometry in Chemical Analysis. p. 385.

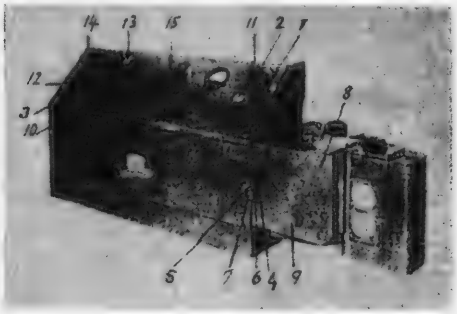
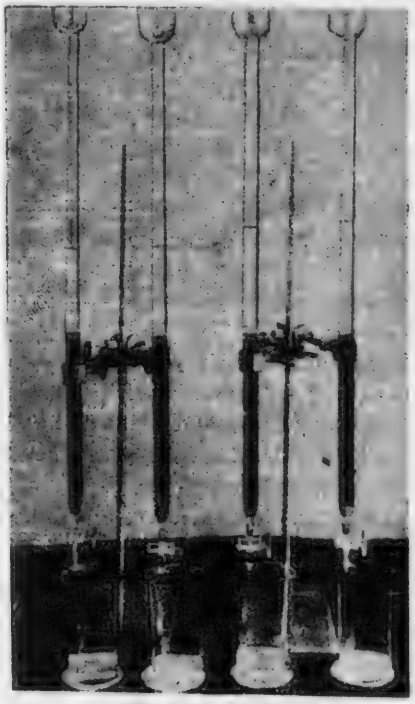


Fig. 3. External appearance of the SF-11 spectrophotometer.
1,2) Handle and scale for the monochromator slit; 3) wave length set up; 8) cell compartment; 9) cell set up in front of the slit; 11) connection for the photoelectric part; 12) regulator for the dark current of the photoelement; 13) wave length scale; 15) handle of the reading potentiometer.

Application of the Ion-Exchange Chromatographic Method in the Analysis of Copper-Iron Ceramic Alloys and Bronzes. p. 417



Apparatus